

CHLORINE NQR STUDIES OF STRUCTURE
BONDING AND MOTION

The experimental results of application of the nuclear quadrupole resonance (NQR) spectroscopic technique to the chlorine nucleus in various series of compounds are presented and discussed.

The chemical bonding of some cyclic inorganic systems is deduced from their Cl^{35} NQR frequencies. The nature of the chlorine bond in series of compounds of acyl and sulphur chlorides is interpreted from their frequencies. In some N-chloro molecules the nitrogen orbital hybridization is deduced and with the assistance of calculations, the N-Cl bond character determined. The results of some compounds with the P-Cl bond are interpreted to yield information of the bonding at phosphorus and in some cases also the molecular structure.

Study of the temperature dependence of the Cl^{35} NQR apparent line-width of the complex, trimethylamine-borontrichloride, is found to complement its reported proton second moment study and is similarly interpreted in terms of molecular motions. The broadening of the Cl^{35} line-widths of trichlorophosphazosulphonyl chloride are similarly interpreted and the respective hindering potentials deduced.

On a présenté et discuté les résultats expérimentaux de résonance nucléaire quadrupolaire (RNQ) appliquée aux noyaux de chlore d'une grande variété de composés.

Les liaisons chimiques sont interprétées à l'aide de leurs fréquences quadrupolaires du Cl^{35} dans différents systèmes cycliques inorganiques. La nature des liaisons chlorées dans les groupements acyl et sulfo-chlorures sont interprétées au moyens des fréquences RNQ. De même, c'est par d'intermédiaire des fréquences RNQ que l'on a pu déduire la nature de l'hybridation des orbitales de l'azote de certains composés N-chlorés. Par la suite et à l'aide de calculs, le caractère de la liaison N-Cl a pu être déterminé. Les résultats obtenus pour quelques composés liaison P-Cl sont interprétés pour donner des informations sur les liaisons du phosphore et aussi dans quelques cas sur la structure moléculaire.

L'étude de l'influence de la température sur la largeur apparente du signal Cl^{35} pour le complexe trichlore de boretriméthylamine vient s'ajouter en accord avec l'étude déjà réalisée sur le moment secondaire de son proton. Ce phénomène est expliqué de la même façon par l'existence des mouvements moléculaires. Ainsi l'étude de l'élargissement des raies correspondantes respectivement aux différents atomes de Cl^{35} du trichlorophosphazosulphonyl chlorure permet de déduire l'intensité de la barrière de potentiel qu'ils possèdent.

CHLORINE NUCLEAR QUADRUPOLE RESONANCE STUDIES OF STRUCTURE,
BONDING AND MOTION IN BORON, CARBON, NITROGEN, PHOSPHORUS
AND SULPHUR CHLORINE BONDS

by

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A Thesis submitted to the Faculty of Graduate Studies
and Research in partial fulfilment of the requirements for the
degree of Doctor of Philosophy.

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July 22, 1970

To: Dr. E.P.A. Sullivan,
a brilliant educator, scientist and humble man
who can make meaningful all phenomena.

His influence was the stimulation for this undertaking.

ACKNOWLEDGEMENTS

Financial Support:

National Research Council of Canada for a Bursary, 1969-70
Graduate Faculty Special Funds for Summer support, 1970.

Assistance:

Russell Boyd for theoretical chemical advice.

Ruth Clipsham for much advice on the chemistry of phosphorus and sulphur, help with syntheses and the bonding interpretation of Chapter II.

Dr. A.J. Frueh for help with the single crystal diffraction work.

Dr. D.F.R. Gilson for drawing on his experience for experimental developments and difficulties, helpful advice on the calculations and interpretation of Chapter III and for the use of his diagrams therein.

Jim Grabenstetter and Jim Pulfer for advice on Hückel parameters.

Dr. M.A. Whitehead for the chemical interpretation of the results, only through his assistance and unremitting enthusiasm this Thesis reached its final form.

Provision of Samples:

Particularly Ruth Clipsham, P. Mathiaparanam and John Larkindale;

Dave Ash, Dr. P. Draper, John Gleason, Paris Georghiou, John Kittredge, Lothar Krause, Dr. J.-P. Montellier, Dimitrios Papaefthimiou, Grant Reader, Phillip Rossy, Dr. S. Shupack, Dr. D. Simkin, Dr. D.E. Young of Allied Chemicals, Morristown, N.J., et alia.

Miscellaneous:

Dr. M. Kaplansky for the early experimental configurations, advice and material for Chapter I and provision of computer programmes.

Fellow student, Lothar Krause, for practical assistance, advice and help with computing and who shared the vicissitudes of this study.

The departmental glassblower, Mr. Stringler, for innumerable vials.

Professor L. St. Pierre for being a temporal godfather.

The committee on Research for the grant for purchase of a Lock-in-Amplifier, without which the work could not have been performed.

The Manuscript:

Joanne Feeney, Dr. M. Forest, Hervé Guérin, John Larkindale and Hilde Schroeder for the typing.

My wife Mary Ann for much support.

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Preface:

Soon after the first report of detection of zero-field quadrupolar interactions in the solid-state it was enthusiastically predicted that NQR studies could potentially provide solutions to the many problems of chemical bonding^{*}. Such statements are still echoed in review articles and after twenty years probation in this respect, the study is fairly summed up as a mataeotechny.

The results of two years of work presented in this Thesis represent a twenty per-cent increase in the number of NQR frequencies of chlorine compounds in the literature. Nevertheless this Thesis does not make Walter Gordy or C.H. Townes prophets, for they failed to indicate how potentially more worthwhile the technique was for studying molecular structure and motion. This is evident in the following chapters.

* see Discussions of the Faraday Society, 19 (1955).

CHAPTER I

Introduction to Nuclear Quadrupolar Resonance Studies

I.1. Introduction

Evidence of the interaction of an aspherical (quadrupolar) nucleus with the surrounding electric field was first recognized in optical spectra in 1935¹. A exhaustive quantum mechanical treatment of this phenomenon was immediately provided². Transitions between the resulting quadrupolar energy levels that appear as hyperfine splittings have subsequently been studied by various spectroscopic techniques³. In 1950 the first report of observation of zero field quadrupolar interactions in solids appeared⁴. Now quadrupolar interaction frequencies have been reported for approximately eleven hundred molecules in the solid state, two-thirds of these are for the most abundant chlorine isotope.

There are a number of similar derivations, along classical and quantum mechanical lines, of the non-relativistic Hamiltonian expression for the interaction energy of the nuclear and electronic charge distributions of an n-electron atom^{1,5,6,7}. These are all limited by the same difficulties as they involve separation into two interacting systems of unknown charges the nuclear and electronic contributions to the energy levels that they then express in terms of three parameters: eQ , $e q$ and η , the asymmetry parameter. The quantity eQ , representing the scalar nuclear quadrupole moment, is considered solely a nuclear property independent of the surrounding charge field. It requires an assigned

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value that necessarily must be deduced from observation of this same interaction and thus depends on eQ , the gradient of the surrounding electric field, for it cannot be compared with that of independent methods. Accurate estimation of eQ that is generally considered due to the valence shell electrons associated with the quadrupolar nucleus and regarded as independent of core electron polarization effects is a further problem. Once the origins of the continuous and discrete charge distribution are defined, the potential energy of the Coulombic field is introduced, and hence the applicability of Laplace's equation assumed. Additionally a proper coordinate system must be chosen to give convenient and unique parameters.

No improvements have been made to this model for the Hamiltonian. It is quite sufficient without inclusion of higher-order terms. With inclusion of the assumption of the collinearity of the nuclear magnetic dipole with the quadrupole moment, it accounts excellently for the Zeeman effect resulting from the low-field magnetic perturbation⁸. Most of the attempts at improvement have been in two related areas; the search for better wave functions for atomic electrons or expressions for the charge effective at the nuclear site^{9,10,11} and quantification¹² or circumvention¹³ of the problem of polarization of the core electrons by the nucleus.

A significant attempt has been made to reduce the problem of the observable, (i.e. the transition between energy levels), being the product of a priori unknowns for the case of half-integral spins¹⁴. This was to obtain a more accurate expression for eQ by a classical approach that is claimed to be more accurate than anything hitherto employed. An intrinsic value for eQ is developed from its transformation properties by referring it to a coordinate system of its own principal axis.

I.2. Development of Expressions for the Nuclear Quadrupole Resonance Parameters

The required Hamiltonian expression shall involve only the interactions energy of the third-order nuclear multipole moment with the finite second derivative of the electrostatic potential evaluated at the nuclear site. Such a nucleus has a total ground-state spin angular momentum value I , greater than one-half. The scalar value of its resulting quadrupole moment will be denoted by eQ , where e is the proton charge. The nuclear angular momentum operator $\hat{I}$ has a component along the axis of quantization, z , denoted by I_z . The eigenvalue of $\hat{I}$ is $(I(I+1))^{1/2}$, and of I_z , m , the magnetic quantum number associated with the total nuclear angular momentum, where $m = I, I-1, \dots, -I$.

The Hamiltonian expression for the interaction of the nuclear quadrupole moment tensor $\underline{Q}$, and the electric field gradient tensor $\underline{V}$, is given by their tensor-scalar product¹⁵,

$$\hat{H} = -\underline{Q} \cdot \underline{V}.$$

Laplace's equation is assumed to apply at the nuclear site. From symmetry considerations both these tensors have five independent components and the Hamiltonian matrix components can be expressed in the following manner¹⁶,

$$\hat{H} = - \sum_{m=-2}^2 \underline{Q}^m \underline{V}^{-m}.$$

where

$$Q^0 = A(3 \hat{I}_z^2 - \hat{I}^2),$$

$$Q^{\pm 1} = 6^{1/2} A/2 (\hat{I}_z \hat{I}_{\pm} + \hat{I}_{\pm} \hat{I}_z),$$

$$Q^{\pm 2} = 6^{1/2} A/2 \hat{I}_{\pm}^2,$$

$$V^0 = 1/2 V_{zz},$$

$$V^{\pm 1} = -1/6^{1/2} (V_{xz} + i V_{yz}),$$

$$V^{\pm 2} = 1/2 \cdot 6^{1/2} (V_{xx} - V_{yy} \pm 2i V_{xy}),$$

and where

$$A = \frac{eQ}{2I(2I - 1)},$$

$$\hat{I}_+ = \hat{I}_x + i\hat{I}_y,$$

$$\hat{I}_- = \hat{I}_x - i\hat{I}_y.$$

It is possible to choose a generalized set of coordinates such that the off-diagonal terms of the symmetric traceless electric field gradient (e.f.g.) tensor vanish. This set is termed the principal axis-system of the e.f.g., and,

$$V^0 = 1/2 eq,$$

where e is the unit of electronic charge. The Hamiltonian can then be expressed as,

$$\hat{H} = \frac{eQ}{2I(2I - 1)} (V_{xx} \hat{I}_x^2 + V_{yy} \hat{I}_y^2 + V_{zz} \hat{I}_z^2).$$

Further the principal axes are so selected that

$$|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|,$$

and

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}.$$

The dimensionless quantity η , the asymmetry parameter, defines the deviation of the e.f.g. along the principal axis z , from axial symmetry. Hence the Hamiltonian can further be expressed as,

$$\hat{H} = \frac{e^2 Qq}{4I(2I-1)} ((3 \hat{I}_z^2 - \hat{I}^2) + \eta(\hat{I}_x^2 - \hat{I}_y^2)).$$

The quantity $e^2 Qq$ is termed the quadrupole coupling constant for the nucleus in the particular environment under consideration.

For the situation of the axial symmetry of the e.f.g. the term on the right vanishes and there are no off-diagonal elements. Thus the expectation values can be substituted directly for their operators to yield the energy levels,

$$E_{\pm m} = \frac{e^2 Qq}{4I(2I-1)} (3m^2 - I(I+1)).$$

The power term in m results in a degeneracy of the states. For half-integral I there are $I + 1/2$ doubly degenerate energy levels, whereas for integral I ; $I + 1$ energy levels, I being doubly degenerate, with the one exception of the lowest state, $m = 0$.

In the absence of axial symmetry the Hamiltonian expression requires a diagonalization procedure for solution. The term in η introduces the operators $\hat{I}_x^2$ and $\hat{I}_y^2$ that mix the states differing by $\Delta m = 2$, thus incurring off-diagonal terms in the Hamiltonian matrix. Typical expressions for the eigen-states of the submatrices are available¹⁶ and also the secular equations for half-integral values of I evaluated in closed form^{6,17,18}. There is also a treatment of integral values of I ¹⁹.

Since these studies are mostly concerned with observation of the $I = 3/2$ transitions, its case will be considered further¹⁶. The Hamiltonian is a four-by-four matrix with non-zero off-diagonal terms in η . It reduces to two identical submatrices as the levels differing only in the sign of m are degenerate. Diagonalization yields the following expression for the secular equation,

$$E^2 - 3\eta^2 - 9 = 0,$$

that can be solved exactly for the two energy eigenvalues:

$$E_m = \pm 3/2 = 3eqA/2 (1 + \eta^2/3)^{1/2},$$

$$E_m = \pm 1/2 = -3eqA/2 (1 + \eta^2/3)^{1/2}.$$

Transitions between these energy levels can be initiated by electromagnetic radiation if it obeys the Einstein-Bohr condition, $\Delta E = h\nu$. The selection rule for these transitions is $\Delta m = \pm 1$. The expression for the observable ν_{res} , in frequency units is,

$$\nu_{res} = |e^2 Qq / 2h (1 + \eta^2/3)^{1/2}|$$

Thus for the case of $I = 3/2$ the energy levels are doubly degenerate in m , hence in other than the a priori unknown situation of axial symmetry, the quadrupole coupling constant cannot be determined from the transition frequency alone. This would require a determination of the asymmetry parameter through the application of a weak magnetic perturbation¹⁵, accounted for by inclusion of additional terms in the Hamiltonian expression¹⁶. In no way can the sign of the quadrupole coupling constant be determined from these experiments.

In this development it has been shown that the components of the nuclear quadrupole interaction tensor are completely defined by five parameters, e^2Qq , η and the three angles describing its relative orientation with respect to its principal axis system. The desideratum of the experiment is the determination of eq which is frustrated by the lack of a value for eQ .

I.3. Theory of the Temperature Dependence of the Frequency.

The quadrupole coupling constant in the solid at constant pressure typically exhibits a temperature coefficient of about $-4 \times 10^{-4} \text{ deg}^{-1}$. The low frequency vibrational bands of solids in the region of a few hundred wave numbers, are assignable to intra molecular torsional oscillations or librations. The frequencies of these motions exceed the NQR frequency by a factor of as much as one thousand. Thus the e.f.g. experienced by the quadrupolar nuclei is averaged over these motions and reduced from that

expected for the static lattice. With increasing temperature the amplitudes of the motions increase, consequently the NQR frequency is reduced. This concept is the basis of the Bayer theory²⁰ of the temperature dependence of the NQR frequency, it has been generalized by Kushida²¹ to include motion about any axis.

A quantitative expression for this averaging of the NQR frequency can be developed in the following manner. Consider a quadrupolar nucleus of an atom in an e.f.g. at a site of axial symmetry, librating about the three principal axes. These axes, fixed in space, will be denoted as (x,y,z), and another set attached to the librating atom, by (x',y',z'). Additionally, θ_x, θ_y and θ_z will denote the respective interaxial angles.

Since it is the e.f.g. of the primed axis system that yields the observable, derivation of an expression for the temperature dependence will be necessary. Thus its e.f.g. tensor $\underline{V}'$ must be related to that of the fixed system, $\underline{V}$. It has been shown²² that where $\underline{T}$ is the transform matrix from the coordinate system, (x,y,z) to (x',y',z'), the following expression relates $\underline{V}'$ to $\underline{V}$,

$$\underline{V}' = \underline{T} \underline{V} \overline{\underline{T}},$$

$\overline{\underline{T}}$ denoting the transpose of $\underline{T}$. Since both coordinate systems have the same origin, $\underline{T}$ can be constructed from the matrices, $\underline{T}_x, \underline{T}_y$ and $\underline{T}_z$, corresponding to rotations about the x,y and z axes and it will be equal to their matrix product.

The instantaneous e.f.g. tensor for the librating atom is non-diagonal and time-dependent, so the time averaged terms of θ_i etc., e.g., $\overline{\theta_i}$ must be introduced. Obviously $\overline{\theta_x} = \overline{\theta_y} = \overline{\theta_z} = 0$ and it follows that the averaged e.f.g. tensor is diagonal.

The components of $\underline{V'}$ can be written in the following form,

$$\begin{pmatrix} V'_{xx} \\ V'_{yy} \\ V'_{zz} \end{pmatrix} = \begin{pmatrix} 1 - \overline{\theta_y^2} - \overline{\theta_z^2} & \overline{\theta_z^2} & \overline{\theta_y^2} \\ \overline{\theta_z^2} & 1 - \overline{\theta_x^2} - \overline{\theta_z^2} & \overline{\theta_x^2} \\ \overline{\theta_y^2} & \overline{\theta_x^2} & 1 - \overline{\theta_x^2} - \overline{\theta_y^2} \end{pmatrix} \cdot \begin{pmatrix} V_{xx} \\ V_{yy} \\ V_{zz} \end{pmatrix}$$

The principal component of the e.f.g. tensor V'_{zz} , with the assumption of axial symmetry, can be written simply as

$$V'_{zz} = [1 - 3/2(\overline{\theta_x^2} + \overline{\theta_y^2})] V_{zz}.$$

For the case of $I = 3/2$ the NQR frequency of the librating atom, ν' , is given by,

$$\nu' = [1 - 3/2(\overline{\theta_x^2} + \overline{\theta_y^2})] \frac{e^2 Qq}{2h}.$$

It has been assumed that the motion about the x and y axes is identical, thus avoiding the added complexity of there resulting non-axial symmetry of the e.f.g. A further assumption is that motion along the z axis is unimportant, since in most cases it would amount to bond stretching.

Estimation of the magnitude of $\overline{\theta_i^2}$ can be made through treating the motions as quantum harmonic oscillators²³, thus,

$$A_i \omega_i^2 \overline{\theta_i^2} = \hbar \omega_i \left(\frac{1}{2} + \frac{1}{\exp\left(\frac{\hbar \omega_i}{k T}\right) - 1} \right).$$

where ω_i is the torsional frequency, A_i is the moment of inertia of its mode, T the absolute temperature and k the Boltzman constant. Obviously the amplitude of the motion increases with temperature. The above equations together yield,

$$V'_{zz} = V_{zz} \left[1 - \frac{3\hbar}{A\omega} \left(\frac{1}{2} + \frac{1}{\exp\left(\frac{\hbar \omega}{k T}\right) - 1} \right) \right].$$

The relation is more usefully expressed in terms of a frequency, $\nu(T)$, at $T^\circ K$ and for the static lattice,

$$\nu(T) = \nu(\theta) \left[1 - \frac{3\hbar}{A\omega} \left(\frac{1}{2} + \frac{1}{\exp\left(\frac{\hbar \omega}{k T}\right) - 1} \right) \right].$$

This expression fails to account for the effect of lattice expansion with increasing temperature which is understood to result in reduction of the librational frequencies through broadening the potential wells. Brown²⁴ introduced an empirical parameter α , to relate the librational frequency ω at temperature T to that at $0^\circ K$, ω^0 , by,

$$\omega = \omega^0 (1 - \alpha T).$$

The effectiveness of the inclusion of this correction is also possibly due to its ability to accommodate the error due to the observation generally being made at constant pressure, whereas the expression is developed on the assumption of constant volume.

Thus there are two observables for a set of temperature dependent NQR data, $\nu(T)$ and T , and three unknown parameters, $\nu(Q)$, ω and α . The expression is applied to NQR data principally to predict soft lattice vibrational modes presumed effective in the e.f.g. averaging and also to obtain extrapolated NQR frequencies. The usual procedure, as employed in this study, is to solve for best values of the three parameters, by obtaining successively better approximations, through differentiating the equation, in an iterative manner.

I.4. Interpretation of Apparent Thermally Activated Hindered Reorientational Effects in Nuclear Quadrupole Resonance Spectra.

Due to the required detection methods of the weak zero-field quadrupolar interactions in solids, the resulting spectral line-widths invariably contain instrumental components precluding direct interpretation. Further, in the NQR experiment the pure line-width is generally a function of several contributions. Thus pulse techniques are necessary in the determination of the parameters of the various relaxation processes presumed to be effective. Nevertheless, in special circumstances quantitative information can be derived from the direct interpretation of NQR

linewidth data. Two expressions that have been employed will be here presented. These can really only be regarded as empirical, not because of the many assumptions necessary in their derivation but due to the questionable validity of their direct application to the raw experimental data.

Thermally activated hindered rotational effects manifested in NQR spectral line broadening can be related to three physical conditions:

(I), The motional frequency of the rotating group containing the quadrupolar nucleus under study is less than the nuclear precessional (Larmor) frequency. Observed broadening has been interpreted for this case with a simple empirical expression²⁵. For the derivative of a Lorentz-type absorption curve with the line-width taken as the distance between the points of inflexion, denoted by $\delta\nu$, and for a hindering potential energy barrier of V_0 cals per mole, the variation in line-width $d\delta\nu$, with temperature dT , is expressed as,

$$\frac{d\delta\nu}{\delta\nu} = \frac{V_0}{RT} \cdot \frac{dT}{T} \quad (1)$$

The temperature of the maximum of $\delta\nu$ is substituted for T . The evaluation of the left-side of this expression requires the subtraction out of an assumed static or constant contribution to $\delta\nu$. This assumption might be reasonable for small dT but unfortunately $d\delta\nu$ could also contain variation in the dipolar contribution to $\delta\nu$ further to its presumed motional origin.

The second physical condition that this spectral broadening can be related to is;

(II) The frequency of the rotating groups executing jumps between potential energy minima is comparable to the nuclear precessional frequency. An expression developed to describe this case defines a maximum of $\delta\nu$ at the temperature that the average jump-rate is of comparable magnitude to the nuclear precessional frequency²⁶.

This condition is not pertinent to these studies, the third physical condition is,

(III) The motion of the group containing the quadrupolar atom is complete an-isotropic rotation at a frequency in excess of the Larmor frequency. Such a condition has been recognized from the data of these studies so the development of a useful expression will be outlined. For simplicity an axially symmetric e.f.g. will be assumed about an axis, z . Uniform rotation only will be considered to occur about an axis, z' , inclined to z by the angle θ . The space-fixed axes x' and y' together with z' form an orthogonal set at the nuclear site. The instantaneous azimuth of z in the $x'y'z'$ system is denoted by $\phi(t)$. The instantaneous components of the e.f.g. tensor in $x'y'z'$ are given by²⁷,

$$\begin{aligned}
V_{z'z'} &= q/2 (3\cos^2\theta - 1), \\
V_{x'x'} &= q/2 (3\sin^2\theta \cos^2\phi(t) - 1), \\
V_{y'y'} &= q/2 (3\sin^2\theta \sin^2\phi(t) - 1), \\
V_{x'z'} &= q \sin\theta \cos\theta \phi(t), \\
V_{y'z'} &= q \sin\theta \cos\theta \sin\phi(t), \\
V_{x'y'} &= q \sin^2\theta \sin\phi(t) \cos\phi(t),
\end{aligned}$$

where $q = V_{zz}$.

Since the average frequency of rotation is fast compared to the Larmor frequency, it is necessary to average over $\phi(t)$ ²⁶ in order to obtain the quasi-stationary e.f.g. experienced by the nucleus. This is given by,

$$\begin{aligned}
\overline{V_{z'z'}} &= -2 \overline{V_{x'x'}} = -2 \overline{V_{y'y'}} = q/2 (3 \cos^2\theta - 1), \\
\text{and } \overline{V_{x'z'}} &= \overline{V_{y'z'}} = \overline{V_{x'y'}} = 0.
\end{aligned}$$

An axially symmetric e.f.g. along the axis of rotation results,

$$eq' = eq (3 \cos^2\theta - 1)/2.$$

From earlier considerations this expression can be rewritten; if ω is the new frequency value and ω_0 that of the hypothetical static molecule, then their ratio is,

$$\omega / \omega_0 = (3 \cos^2\theta - 1) / 2. \quad (2)$$

Concomitant with such a frequency shift there will be changes in the zero-point motional and non-bonded contributions to the e.f.g. The underlying assumptions in employing such an expression have been thoroughly presented^{26,28}.

I.5. Interpretation of the Character of the Chemical Bond from Quadrupole Coupling Data.

In molecular crystals and the ionic compounds with internally covalently bonded counter ions considered in this study, the e.f.g. about the quadrupolar nucleus originates almost wholly from its valence shell electrons²⁹. That resulting from surrounding charges or neighbouring molecules can be considered minimal in the case of the covalent bond³⁰.

There are a number of approaches, based on approximate methods, to relate the quadrupole coupling constant to the electronic charge distribution of the molecule³¹. These reduce to essentially the same expression that has received widespread acceptance in the interpretation of quadrupole coupling data. In its development here, small magnitude terms representing d-orbital overlap will be ignored and attention will be directed towards the simple case of a halogen-atom bonded to a first row element.

Consider the case of a localized molecular orbital with a terminally bonded halogen atom, that is a sigma bonding orbital being a mixture of s and p_z atomic orbitals. This hybridization leads to a bonding orbital ψ_1 , a doubly occupied orbital ψ_2 along with ψ_4

that are both lone-pair orbitals and an unhybridized p-orbital, ψ_3 , available for pi-bonding. These four valence shell orbitals with their mixing coefficients can now be expressed in the following manner,

$$\psi_1 = s^{1/2} \psi_s + (1-s)^{1/2} \psi_{p_z}$$

$$\psi_2 = (1-s)^{1/2} \psi_s - s^{1/2} \psi_{p_z}$$

$$\psi_3 = \psi_{p_y} \quad \text{and} \quad \psi_4 = \psi_{p_x}.$$

The electron population of both ψ_2 and ψ_4 is two. The occupation of ψ_3 is $(2-\pi)$, where π is the electron loss from pi-type overlap with its bonded neighbour. The population of ψ_1 can be expressed as $(1+i)$ where i denotes the ionic character of the halogen bonding orbital. The fraction of s-character is denoted by s , the degree of s-hybridization.

Substitution of these p-orbital occupations into the following expression³²,

$$\rho = \frac{q_{\text{mol}}}{q_{\text{at}}} = \frac{e^2 Q q_{\text{mol}}}{e^2 Q q_{\text{at}}} = 1/2 (N_x + N_y) - N_z,$$

yields

$$\rho = 1/2(2 - \pi + 2) + (1 - s)(1 + i) - 2s$$

$$\rho = (1 - i)(1 - s) - \pi/2,$$

for the negatively charged halogen atom. Reversal of the first term is parenthesis a necessary for consideration of a positively charged atom.

The pi-electron loss can be related to the asymmetry parameter η , viz.,

$$\eta = \frac{(q_{xx} - q_{yy})}{q_{zz}} = 3/2 \frac{(N_x - N_y)}{\rho}$$

To consider electron loss due to pi-type overlap ($2 - \pi$) can be substituted for N_y

$$\eta = 3/2 \pi/\rho$$

Thus if η is known from experiment or if π is assumed to be zero as is the case of a halogen atom bonded to a saturated system, there is one observable ρ , for the two unknowns, i and s . Townes and Dailey³³ originally made an empirical estimate of s in order that the ionic character could be determined from the observable. There is now available in the literature a complete set of values of s -characters for the chlorine orbital bonded to various atoms³⁴, These have been developed by the electronegativity equalization method.

A particular advantage of the Townes-Dailey expression is that it avoids the necessity of explicit consideration of the effect of core orbital polarization³⁵ that is understood to have a multiplicative effect on the e.f.g. If this is assumed to be equal in both the free atom and also the molecule then it becomes cancelled in the ratio ρ .

In many compounds, chemically equivalent³⁶ quadrupolar atoms exhibit multiplicity in their NQR spectrum. This reflects crystallographic inequivalence of the quadrupolar nuclear sites and sometimes indicates a difference of as great as 5% in their e.f.g. Whilst intermolecular bonding might occur in some compounds in the solid-state nevertheless it is common to observe a 5% to 10% reduction in the quadrupole coupling constant over that of the isolated or gas-state molecule³⁷. Thus the application of the simple Townes-Dailey expression to solid-state NQR data is unrealistic, however by incorporation of a higher s-character, (e.g. 20% as predicted for the solid-state³⁴, instead of the usual 15%), tends to counterbalance these effects.

I.6. Experimental

The experimental studies presented here were performed with two Dean-type³⁸ super-regenerative oscillators, externally quenched by a sine-wave without side-band suppression and with sine-wave frequency modulation. The possibly lesser sensitivity of an externally quenched oscillator over that of a self-quenched one is outweighed by the convenience of operation. Frequency modulation was employed, due to its simplicity and enhanced sensitivity over amplitude modulation, despite its response to spurious interactions. Frequency was scanned by mechanical drive of the variable tuning condensor. A variable d.c. bias³⁹ was applied across the modulation silicon-diode to facilitate manual fine frequency control during NQR frequency determinations. Automatic coherence control was not employed.

Throughout these studies a spectrum-analyzer, (plug-in type, Tektronix Pentrix L20), was employed to very considerable advantage. This was very loosely coupled to the oscillator. It enabled recognition and adherence to the most suitable operating conditions of the oscillator, through the selection of quench rates yielding the most suitable energy distribution of the oscillator spectrum, being invariably when the amplitude of the output was distributed over as few side-bands as possible whilst still maintaining some incoherence. The level of coherence was then controlled by manual adjustment of the grid bias³⁸. Since the characteristics of the oscillators employed are frequency dependent, such control is essential for line-width studies over a temperature range. This method of periodic maintainance of coherence is not that achieved by conventional coherence control systems⁴⁰ that merely sample the overall power output of the oscillator. Of additional importance, the spectrum-analyzer enabled rapid and accurate identification of the oscillator fundamental, that frequently was none of the peaks of the recorded output of the oscillator response.

Oscilloscope display of the oscillator output was not used, but this was fed directly to a lock-in amplifier/phase detector, (Princeton Applied Research Model 121), with only filtering and no pre-amplification. Finally a strip-chart recorder was employed.

This simple experimental arrangement lacks the many sophistications for NQR spectrometers of recent reports^{40,41}. Its lack of automation necessitating continual attention was a small debt for its outstanding success evident in its bountiful performance, not to mention the reduced capital outlay.

Little attention was paid to coil design and sample volumes ranging between 400 mgm to 2 gm sealed in pyrex tubing were employed, depending on the availability of the material. The many commercial products examined frequently required purification by sublimation or distillation before yielding results. These are reported mostly for the temperature of liquid nitrogen, on which periodic checks were made, using a variety of thermocouples, that indicated it to be at $(77.0 \pm 0.5)^{\circ}\text{K}$ whenever it was reasonably free of dissolved gases or ice. Solid samples were always lowered into liquid nitrogen over a period of at least one day to reduce the possible presence of lattice strains or disorder. In the case of liquids or gases care was taken to ensure that crystallinity resulted on cooling, this sometimes required considerable patient manipulation.

When an interaction recognized in the recorder output had been related to a peak on the spectrum-analyzer and the d.c. bias on the modulation circuit adjusted for its centre, then the transmission of a loosely-coupled BC 221 frequency meter would be superposed on the respective peak of the spectrum-analyzer to yield a precise frequency measurement. Thus zero-beat could be recognized both visually and aurally. A direct-reading signal generator was employed to check the harmonic identification of the frequency meter. Periodically the accuracy of the BC 221 frequency meter was checked against various frequency counters and also a precalibrated frequency meter. Its apparent accuracy was always limited to the reading error of its dial vernier. Thus it was possible to determine a NQR frequency to an absolute accuracy of $\pm 100 \text{ H}_2$ if the line-width was not

not in excess of 5 kHz . Considering however that the absolute accuracy of the temperature determination is limited to ± 0.5 degree at low temperatures and that the temperature dependence of the NQR frequencies here observed was about -3 kHz deg^{-1} , then the frequency could have an error of $\pm (1.5 \text{ to } 2.0) \text{ kHz}$.

The few compounds that gave particularly intense lattice elastic effects or were of a non-centrosymmetric crystal class, as deduced from their interaction with the frequency modulation, were examined with a DECCA NQR spectrometer using Zeeman modulation. This became available at the completion of these studies. The results are also included in their respective sections.

ADDENDA

Addendum I, The Sternheimer Effect.

Throughout this Thesis the effect of possible variation of the magnitude of Sternheimer's factor^{1,2} for core polarization in the chlorine atom is ignored. Nevertheless the magnitude of this process will depend on the distribution of the bonding electrons about the quadrupolar nucleus. Qualitative bonding information from single temperature NQR frequency observations is elucidated in this work, by comparisons mostly within series of molecules having the quadrupolar nuclei under consideration in an identical bonding situation. It is for this reason that no consideration has been taken for possible variation in the magnitude of this factor. Where comparisons have been made amongst different series of molecules, neglect of this variation is a possible deficiency.

1. Reference 12 of Chapter I.
2. Reference 3 ibid., Chapters 5 and 6.

Addendum II, Identification of the Compounds Studied.

Chapter II. The three samples employed were identified by spectroscopic studies, elemental analysis and their physical properties, that are together tabulated in the publication of the preparation and properties of the title compound of this Chapter. This is referenced in II.1.

Chapter III. Samples of the title compound were identified by their infra red spectra. Their elemental analyses and physical properties were in accordance with the preparative procedure referenced in III.2.

Chapter IV. Samples of the title compound were prepared following the standard procedure referenced in IV.2. These were identified by their infra red spectra and by melting-point determination.

Chapter V. The phenylchlorophosphoranes were identified by their infra red spectra, by melting-point determination and elemental analysis. The cyclic phosphorus esters and phosphates were all of commercial origin. Whenever possible their melting points were determined and compared to their respective Literature values. The compounds with the trichlorophosphazo group were prepared and identified by their infra red spectra and elemental analyses.

Chapter VI. Table 2: Four of the compounds were of commercial origin and were either sublimated or distilled under the conditions described in the Literature. Each was identified by at least one physical property and also by its infra red spectrum. The remaining compounds of Table 2 were prepared as intermediates and borrowed for NQR investigation. Table 3 and 4: All samples were of commercial origin and were accepted as labelled. Table 5: The first compound was prepared following the listed reference and identified by its infra red spectrum and melting-point. Tables 6,7,8,and 9: The samples were of commercial origin, the liquids were accepted as labelled, the others were purified by sublimation and their melting-points checked against their Literature values.

Chapter VII. The one liquid studied was of commercial origin and accepted as labelled, the solids were sublimated and their melting-points checked against their Literature values.

Chapter VIII. The compounds of Table 1 and 2 were of commercial origin and accepted as labelled, those of Table 3 were checked by one physical property.

Appendix. All compounds of Table 1 were of commercial origin and accepted as labelled. Cl_8BP was identified by its infra red spectrum and melting-point, Cl_9SSb ; similarly by its infra red spectrum, melting-point and by elemental analysis. Selenyl chloride was of commercial origin and accepted as labelled.

CHAPTER I

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CHAPTER II

Chlorine Nuclear Quadrupole Resonance of some Cyclic

Inorganic Compounds

II.1. Discussion of the Compounds and their Chlorine NQR Spectra.

There has been considerable interest in the structure and properties of cyclic phosphonitrilic halides, though no consensus has been reached concerning the bonding involved in such compounds. Cyclic trimeric sulfanuric halides have also been reported and characterized. Cyclo- μ -nitrido-dichlorophosphorus bis(oxochlorosulphur), $\text{NPCl}_2(\text{NSOCl})_2$, can be thought of as a ring composed of units of both types and this has been confirmed in the X-ray study¹. The work discussed in this chapter was performed during the course of investigation into the preparation and characterization of such mixed rings in an attempt to gain further insight into the bonding involved in inorganic compounds containing phosphorus and/or sulfur atoms.

$\text{NPCl}_2(\text{NSOCl})_2$ was prepared as reported by Clipsham, Hart and Whitehead². A single crystal X-ray structural analysis was commenced and $\text{hn}\ell$ data collected with a Weissenberg camera after the space group $\text{P2}_1/\text{n}$ and the lattice parameters were determined using a precession camera. Work was discontinued after Acta Crystallographica listed similar work, to be published. Communication with the authors Drs. J.C. Van de Grampel and A. Vos and exchange of $\text{hl}\ell$ data confirmed the assigned space group and lattice parameters, and that this compound was the subject of their structural analysis.

α -(NSOCl)₃ and β -(NSOCl)₃. Samples of these sulfanuric chlorides were prepared from pyrolysis of trichlorophosphazenesulfonyl chloride as described by Vandi, Moeller and Brown³. A sample of the β form obtained from a separation by vacuum sublimation was used without recrystallization. Samples of the α form were purified by recrystallization from n-hexane. Both forms were confirmed by comparison of their infrared spectra with those reported³.

The Cl³⁵ NQR spectra in Table 1 are listed at room temperature as well as 77°K in order to approach the temperatures of the available X-ray structural analyses. The spectrum of the mixed ring consists of four intense interactions of equal magnitude. A further four weaker interactions are attributable to Cl³⁷. Considering the Cl³⁵ room temperature NQR spectra of cyclic trimeric phosphonitrilic chloride, (NPCl₂)₃, and the α form of sulfanuric chloride, α -(NSOCl)₃, enables the interactions observed for the mixed ring to be identified with the phosphorus and sulfur chlorine atoms of the molecule. The frequency of the weighted average of the nuclear quadrupole interactions of (NPCl₂)₃ is 27.745 MHz. The weighted average of the interactions of α -(NSOCl)₃, is 36.243 MHz. Thus the lower frequency pair of interactions results from chlorines bonded to the phosphorus atom and the higher frequency pair of interactions from chlorines bonded to the two sulfur atoms of the mixed ring molecules.

TABLE 1

Frequencies in MHz of the Cl^{35} Nuclear Quadrupole Interactions of
some Cyclic Inorganic Compounds ^a

$\text{NPCl}_2(\text{NSOCl})_2$	$\alpha\text{-(NSOCl)}_3$	$\beta\text{-(NSOCl)}_3$ ^b	$(\text{NPCl}_2)_3$ ^c
28.660	36.138*	36.134	27.880*
29.836	36.454	36.445	27.812
34.521		37.55	27.684
35.472			27.608*
<u>Data of 77° K</u>			
29.339	36.996*	37.149	28.684
30.484	37.227	37.354	28.598
35.226		38.416	28.318
36.358			28.328

^a All interactions for each compound are of equal intensity except those marked with an asterisk which are of twice the intensity of the others for that compound. ^b As the temperature of observation approaches the melting point (320°K), the interactions become less sharp and lose intensity. The highest frequency interaction is particularly affected.

^c Reference 13 .

The X-ray structural analysis ¹ showed that molecules of $\text{NPCl}_2(\text{NSOCl})_2$ are in a distorted chair configuration with both sulfur

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^c Reference 13 .

The X-ray structural analysis¹ showed that molecules of $\text{NPCl}_2(\text{NSOCl})_2$ are in a distorted chair configuration with both sulfur

chlorine substituents axial, (see Figure 1). The most striking feature is the considerable distortion from Cs molecular symmetry resulting from intermolecular interactions between exocyclic atoms. If the molecule possessed Cs symmetry, the chlorines bonded to the sulfur atoms would be chemically equivalent, whereas those bonded to the phosphorus atom would not. Thus the observation of two separate phosphorus chlorine frequencies and also two separate frequencies from the chemically equivalent sulfur chlorines is in agreement with the solid state structural determination¹. The multiplicity of the sulfur chlorine frequencies results from intermolecular interaction reflected in molecular distortion from Cs symmetry.

II.2 Discussion of the Temperature Dependence of the NQR Spectrum of $\text{NPCl}_2(\text{NSOCl})_2$.

The NQR data collected between liquid nitrogen and room temperature of the four interactions was fitted to a curve in order to estimate the resonance frequencies for absolute zero and also for the rigid lattice.

Curve fitting of temperature dependent NQR data can yield significant information of molecular motion and to the correct assignment of vibrational spectral bands from the lattice vibrational modes⁴. However the complete analysis requires a knowledge of all the torsional and vibrational modes, their degeneracy and also their characteristic inertial and frequency factors. For planar molecules or those possessing

symmetry axes intersecting their centre of gravity, estimation of inertial factors for torsional modes is possible. However for $\text{NPCl}_2(\text{NSOCl})_2$ this is a very considerable task. Considering its low molecular symmetry and the absence of knowledge of the low frequency vibrational spectrum, a simple model was employed, merely regarding the cyclic molecular framework as being fixed, with the exocyclic chlorine atoms executing torsional oscillations in a plane lying perpendicular to these respective bond axes. These axes were further considered to be coincident with the principal axes of the e.f.g. tensor. The effect of a finite asymmetry parameter and thus its temperature dependence was ignored. The values for the moments of inertia of the chlorine atoms were determined from the structural determination¹. The fit of the NQR data was achieved through an iterative process on the McGill IBM/360/75 machine, convergence was rapid almost irrespective of the magnitude of the guessed starting parameters. The programme is described in the literature⁵.

The temperature dependent NQR data for $\text{NPCl}_2(\text{NSOCl})_2$ and the curve from the Bayer-Kushida-Brown treatment is displayed in Figure 2, and the results are listed in Table 2. The low intensity of the interactions, their appreciable line-width and the imprecision of the temperature determination causes scatter. Considerable reduction in the root-mean-square deviation was achieved by neglecting the data below 100°K in the fit, this also resulted in a common value for the correction factor due to Brown for the four lines, of about $4 \times 10^{-4} \text{ deg}^{-1}$, in agreement with literature values for similar molecular crystals⁵. This result suggests that there is a slight change in the gradient of the temperature dependence of the NQR frequencies just below 100°K , indicating that a

TABLE 2

Results of Fitting the NQR Data to the Bayer-Kushida-Brown Temperature Dependence Curve

	NQR data for $\text{NPCl}_2(\text{NSOC1})_2$				ditto; excepting data below 100°K			
Respective atom	Cl(1)	Cl(2)	Cl(3)	Cl(4)	Cl(1)	Cl(2)	Cl(3)	Cl(4)
Moment of Inertia, 10^{-37} gm cm^2	0.226	0.226	0.240	0.240	0.226	0.226	0.240	0.240
Brown's factor, $\text{deg}^{-1} \times 10^{-4}$	-0.7099	2.202	3.939	4.034	4.406	5.200	4.447	5.546
Librational frequency, cm^{-1}	70	80	85	78	87	92	87	83
Rigid lattice NQR frequency, MH_z	29.572	30.680	35.419	36.592	29.463	30.616	35.409	36.550
Absolute zero NQR frequency, MH_z	29.418	30.538	35.273	36.428	29.337	30.492	35.266	36.396
Root-mean-square deviation, kHz	18	12	10	13	9	5	8	6

reordering of the crystal lattice and change in the dominant lattice vibrational modes occurs. To investigate this further, the data below 100°K needs extending, to provide sufficient for curve fitting to establish this apparent phase transition.

In view of this evidence that the bulk of the NQR data represents a high temperature phase, discussion of the frequencies predicted for absolute zero and for the rigid lattice is of questionable value. It is however interesting that a pair of these predicted frequencies differs by as much as 150 kHz, compared with a typical difference of about 30 kHz for the similar phosphonitrilic chloride molecules⁵. This prediction and the fact that these interactions exhibit a temperature coefficient of NQR frequency of only $-103 \times 10^{-6} \text{ deg}^{-1}$ compared with about $-120 \times 10^{-6} \text{ deg}^{-1}$ in the phosphonitrilic chlorides over the same temperature ranges, indicates that even at 77°K they are already considerably averaged. This is in good agreement with the findings of the structural determination of the molecule¹ which revealed large amplitude molecular motions.

The predicted librational frequencies effective in the e.f.g. averaging for the apparent high temperature phase are close. This result is encouraging, for although these are associated with the oscillations of atoms in two different chlorine bonds and thus differing restoring forces, the terminal atoms are of identical mass. Experiment could confirm the predicted frequencies, but their narrow frequency region will be further complicated by another set of four weaker bonds at slightly lower frequency due to the less abundant chlorine isotope.

II.3 Chemical Interpretation of the Bonding in $\text{NPCl}_2(\text{NSOCl})_2$

In the process of structural refinement¹ it was found that considerably larger corrections for thermal motion were required for two of the chlorine atoms, (Cl(1) and Cl(4)), than the corrections calculated using the rigid body approximation. At a given temperature, nuclear quadrupole interaction for two chlorine atoms in equivalent bonding situations but otherwise inequivalent environments (i.e. inequivalent non-bonding situations) should be separated by a frequency difference proportional to the relative amount of thermal averaging of the e.f.g. at each nucleus. Contributions to the e.f.g. either direct or indirect, from the non-bonded environment, become important only in ionic crystals⁶. Considering the relative slopes and positions of the plots of NQR frequencies versus temperature for the $\text{NPCl}_2(\text{NSOCl})_2$ (Figure 2) for the two pairs of interactions, it is possible to relate the higher frequency phosphorus chlorine interaction to Cl(1).

These assignments will now be discussed in terms of current chemical concepts. The Townes-Dailey theory⁷ of nuclear quadrupole coupling considers the major contributions to the e.f.g. within the framework of the LCAO-VB approximation. An increase in chlorine s character, and an increase in ionic character of the sigma bond to a chlorine atom results in a reduction of the frequency of the quadrupolar interaction. Any π bonding involving the doubly filled chlorine valence atomic orbitals would reduce the e.f.g. at the chlorine nucleus thus further reducing the frequency.

To a first approximation the sigma bond hybrids at either a phosphorus or a sulfur atom in a ring system such as $\text{NPCl}_2(\text{NSOCl})_2$ are tetrahedral. The electronegativity of a phosphorus tetrahedral hybrid is lower than that of a sulfur tetrahedral hybrid⁸, hence a phosphorus chlorine bond would be more ionic than a sulfur chlorine bond, and the frequency of interaction for phosphorus chlorines would be lower than that of sulfur chlorines. An estimation of the departure from sp^3 hybridization at the central atom can be made from a consideration of the determined bond angles. Reduction of the exocyclic angle from 109.4° at a ring phosphorus or sulfur atom reflects a decrease in s character of the central atom exocyclic hybrids. The electronegativity of a hybrid of s and p orbitals, decreases with decreasing s character⁸, thus reduction of the exocyclic angle leads to lower $\text{Cl}^{35}\text{ nqr}$ frequency. A comparison of the exocyclic angles for $\text{NPCl}_2(\text{NSOCl})_2$, $(\text{NPCl}_2)_3$ and $\alpha\text{-(NSOCl)}_3$ indicates that there are slight differences which may account for the difference in average frequencies of the S and P chlorines. The average $\text{Cl}\hat{\text{P}}\text{Cl}$ angle in $(\text{NPCl}_2)_3$ is 102° ⁹ while the $\text{Cl}\hat{\text{P}}\text{Cl}$ angle in $\text{NPCl}_2(\text{NSOCl})_2$ is 104.4° . The $\text{O}\hat{\text{S}}\text{Cl}$ angles in $\alpha\text{-(NSOCl)}_3$ and an $\text{NPCl}_2(\text{NSOCl})_2$ are 108° ¹⁰ and 106° , respectively. Thus the interactions for the mixed ring phosphorus chlorines should occur at a higher average frequency than those observed for $(\text{NPCl}_2)_3$ and the interactions for the sulfur chlorines should occur at a lower average frequency than those for $\alpha\text{-(NSOCl)}_3$, this is observed. It is therefore apparent that a sigma bond inductive effect is present.

The endocyclic bonding in such cyclic inorganic compounds is complex and has recently been described by Mitchell¹¹. It is characterized by π and π' systems in addition to the sigma bonding. Exocyclic π bonding (discussed subsequently) will be in competition with the π and π' systems. Evaluation of the magnitude of the asymmetry parameter at the Cl atom is unlikely to yield further information on the bonding as both the Cl lone pair orbitals can become involved in the exocyclic π bonding according to symmetry considerations.

It has been customary to consider differences between observed NQR frequencies of 3% or more of their average to reflect chemical inequivalence and those of 1% or less to reflect crystallographic inequivalence¹². The Cl³⁵ NQR spectrum of α -(NSOCl)₃ shows a single interaction and another half as intense separated by 0.316 MHz (0.87%). This is in agreement with the solid state structural determination¹⁰ which places two-thirds of the chlorine atoms per unit cell in a different crystallographic site from the remaining third although all chlorine atoms are chemically equivalent. The Cl³⁵ NQR Spectrum of β -(NSOCl)₃, Table 1, shows three interactions of equal intensity; two are closely spaced and the third is much further removed. It is thus consistent with the suggestion of Vandt, Moeller and Brown³, inferred from dipole moment studies, that the molecular configuration is chair with two chlorines axial and one chlorine equatorial. However, since in the mixed ring the relatively large separation of the sulfur chlorine interactions results from crystallographic effects rather than chemical inequivalence, this criterion cannot be universally applied.

The frequency separations of both pairs of interactions in the mixed ring are relatively large compared with those of α -(NSOCl)₃ and (NPCl₂)₃ or (NPCl₂)₄^{13,14}. In solid state NPCl₂(NSOCl)₂ there is a significant difference in the two sulfur chlorine interatomic distances (S(1) - Cl(3) 2.007^oÅ, S(2) - Cl(4) 2.028^oÅ) reflecting a difference in the bonds resulting from the distortion from Cs symmetry. The Cl³⁵ nuclear quadrupole coupling constant has been observed to increase with increasing bond length for predominantly covalent bonds due to a decrease in chlorine s character and in sigma bond ionic character¹⁵. While the magnitude of this effect is unknown for the sulfur chlorine bond it has been shown to be considerable for a carbon chlorine bond and is thus capable of accounting for the separation observed between the sulfur chlorine interactions of the mixed ring.

The phosphorus chlorine interatomic distances are identical within the limits of error. Dixon et al¹⁴ have assigned the interactions observed for the two known forms of (NPCl₂)₄ on the basis of varying amounts of exocyclic π bonding estimated from the "polar" angle between the exocyclic bond and the direction perpendicular to the plane of the ring segment NPN. The angle determines the amount of overlap between occupied chlorine p orbitals and suitably oriented unoccupied phosphorus d orbitals. For example, "polar" angles calculated for the chair form¹⁶ of (NPCl₂)₄ are: Cl(1) 43.9°, Cl(2) 32.8°, Cl(3) 40.4°, Cl(4) 37.0°, and the room temperature interaction frequencies (in MHz) can be assigned as: 27.224, 28.597, 28.093 and 28.150, respectively¹³. The "polar" angles for the mixed ring phosphorus chlorines are: Cl(1) 39.0° and Cl(2) 36.0°. The assigned frequencies are 28.660 MHz and 29.836 MHz, respectively. Any π effect is thus

in the correct direction to explain the separation. However, in $(\text{NPCl}_2)_4$ for example, separations of 1.373 and 0.057 MHz are related to "polar" angle differences of 11.0° and 3.1° , whereas for the mixed ring the separation of 1.176 MHz must be related to an angle difference of 3.0° . The relative positions of the interactions for $\alpha\text{-(NSOCl)}_3$ cannot be accounted for by invoking similar π bonding involving the chlorine atoms. As has been noted, these interactions can be assigned unambiguously from the intensity ratios. The "polar" angles calculated for $\alpha\text{-(NSOCl)}_3$ (Cl(1) 30.1° , Cl(2) 31.4°) would place the interactions in the reverse order to that observed. Therefore the effect, if it occurs, must be masked by some opposing effect.

Another possible explanation of frequency separations within chemically equivalent groups of chlorines could lie in differences in thermal averaging of their e.f.g's reflecting crystal packing effects. A measure of mean square amplitude of vibration, $\overline{u^2}$, in a given direction for an atom can be determined from the anisotropic thermal parameters, U_{ij} , found from a structural refinement according to Cruickshank¹⁷.

$$\overline{u^2} = \sum_i \sum_j U_{ij} l_i l_j$$

where $l = l_i, l_j, l_k$ is a unit vector defining the direction of vibration. Choosing directions of vibration along the bond to a particular chlorine atom, perpendicular to the plane defined by the exocyclic substituents and the atom to which they are bonded, and perpendicular to the bond to the chlorine in this plane, values of $\overline{u^2}$ for each chlorine atom were determined. A qualitative comparison of the "net motion" of each

chlorine atom with respect to that of the atom to which it is bonded in the same directions leads to the conclusion that the thermal motion of Cl(1) is greater than that of Cl(2) for $\text{NPCl}_2(\text{NSOCl})_2$. From similar calculations for $(\text{NPCl}_2)_4$ and $\alpha\text{-(NSOCl)}_3$ based on the U_{ij} values reported for the structural refinements^{9,16}, the observed NQR interactions can be assigned to particular chlorine atoms. For $(\text{NPCl}_2)_4$, the assignment and relative separations fall in the same pattern as that based on the π effect¹⁴. In addition, the separation and relative position of the two interactions observed for the crystallographically inequivalent chlorines of $\alpha\text{-(NSOCl)}_3$ can be explained on this basis.

Thus, both a π effect and consideration of relative thermal averaging fit the assignment of phosphorus chlorine interactions, while the π effect alone cannot explain the assignment for the sulfur chlorines in these ring compounds.

It must be noted that relative thermal averaging calculated for Cl(3) and Cl(4) of $\text{NPCl}_2(\text{NSOCl})_2$ would position the interactions assigned to these chlorines in the reverse order, implying that the difference in bond lengths in this case is of much greater importance in determining interaction frequencies.

Chapter II

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CHAPTER II

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- Figure 1. Molecule of $\text{NPCl}_2(\text{NSOCl})_2$. The black solid circles designate oxygen atoms.
- Figure 2. Plot of the Cl^{35} NQR frequencies of $\text{NPCl}_2(\text{NSOCl})_2$ versus temperature. The continuous line is the curve of the fitting of the data above 100°K to the Bayer-Kushida-Brown theory. The dashed line represents the extrapolated values of the fit.

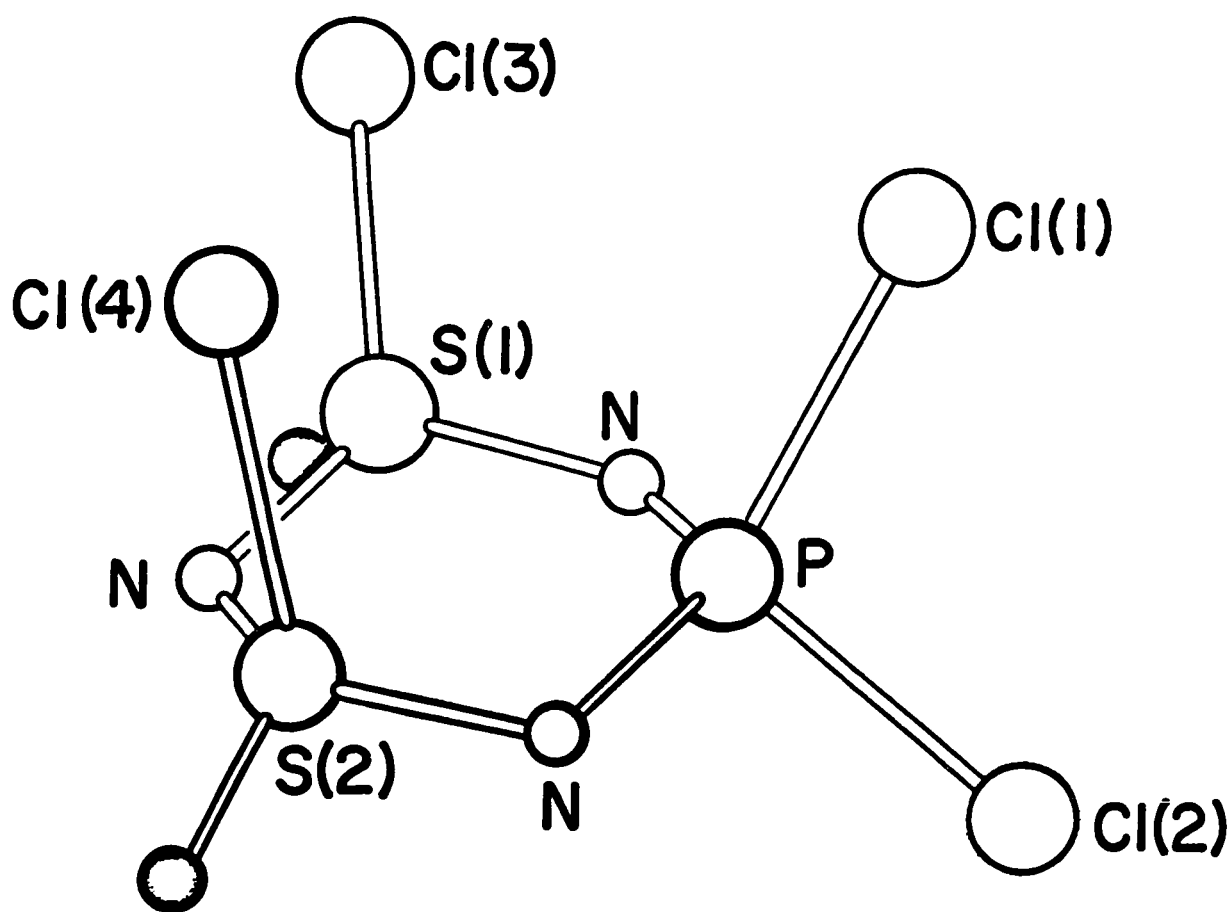
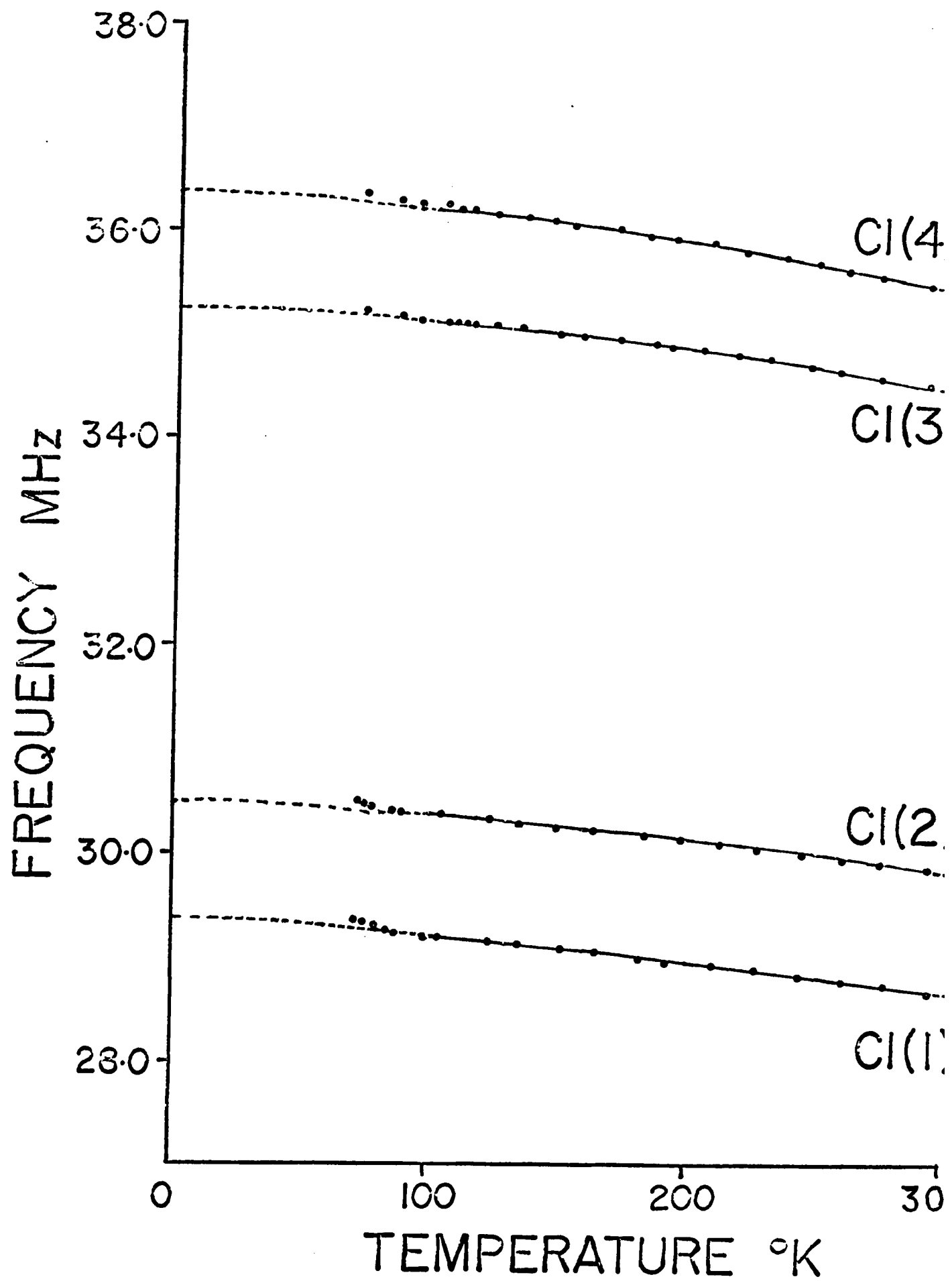


FIGURE 1



CHAPTER III

Investigation of Molecular Motion in Trichlorophosphazosulphuryl Chloride

III. 1. Introduction

It is well known that NQR relaxation experiments can yield detailed and significant information of molecular motions and their onset¹. Quantitative evaluation of dynamical and thermodynamical data of lattice dynamical and of molecular motional processes from magnetic resonance employs the expressions of Bloembergen, Purcell and Pound². The knowledge of the spin-spin and spin-lattice relaxation times, and free induction decay time for the nuclear spin system, from steady-state and pulse experiments and thus complex experimental arrangements are required, particularly for the case of nuclei other than protons.

Sensitive detection of NQR requires the use of super-regenerative oscillators (s.r.o) that yield complex and distorted line shapes³. However by operation at a constant power level and minimal level of modulation a s.r.o. yields line-widths which are functions of molecular motion. Thus, by studying the NQR apparent line-width with respect to temperature, the observation and at least quantitative estimation of thermodynamical values of molecular motional processes is feasible.

Ayant⁴ and Buyle-Bodin⁵ first described studies of the effects molecular torsional oscillations on NQR line-width after Bayer provided the general theory of averaging of the electric field gradient (e.f.g.) by molecular motions⁶. Their interpretation is based on the concept of

of life-time broadening. The molecular reorientational motion is considered to produce a fluctuating e.f.g. at the quadrupolar nucleus which induces transitions between nuclear energy levels limiting the life-time and thus broadening the spectral lines.

The effective molecular motion in the NQR experiment is unlikely to be complete molecular rotation but rather reorientation of groups about their equilibrium positions. Each reorientating unit can be understood to exist in a cage of neighbours that form a complex potential well⁷. The potential barrier hindering rotation will also result from the intra-molecular restraints of covalent bonding and steric hindrance.

III.2. Experimental

Even with preamplification the Cl^{35} NQR interactions studied in $\text{Cl}_3\text{PNSO}_2\text{Cl}$ were too weak to be observed with oscilloscope display. Therefore line-width determination was performed by comparison of the recorder output against a precalibrated scale. The line-width was taken as the signal width at half-height. The validity of the line-widths thus determined was established by measuring the line-widths of some samples having reported values: A powder sample of reagent grade sodium chlorate at 0°C gave a line-width of 1.6 kHz for the Cl^{35} interaction, c.f., 1.4 kHz with a marginal oscillator at that temperature⁸, in a powder sample of commercial Cu_2O at room temperature, the Cu^{65} interaction had a line-width of 12.8 kHz, c.f., 20 kHz with a s.r.o at that temperature⁹; a polycrystalline sample of unpurified para dichlorobenzene at room temperature had a Cl^{35} line-width of 1.5 kHz, c.f., 1.4 kHz at that temperature¹⁰.

The temperature of the sample and surrounding tank circuit coil, enclosed in a heavy copper cavity, was monitored with an uncalibrated copper-constantan thermocouple and Rubicon potentiometer, using the temperature of thawing distilled water as reference. It is desirable to have the junction within the sample, but this was precluded by the sample's reactivity. The temperature measurements are reproducible to $\pm 0.2^{\circ}\text{C}$ with an absolute accuracy of 0.5°C . The thermal gradient over the sample was not considered to contribute to the line-width, and no correction was made for the terrestrial magnetic field. Temperature variation and control were achieved by positioning the copper cavity in or above either liquid nitrogen, or slushes of isopentane-liquid nitrogen, of pentane-liquid nitrogen and of ethanol-dry-ice. Imprecision in the temperature determination causes the scatter of the points in the figure. The temperature was cycled in both directions to cancel possible lag.

The sample of $\text{Cl}_3\text{PNSO}_2\text{Cl}$ was prepared by Dr. Ruth Clipsham following the reported procedure¹¹. It was repeatedly pressed and filtered under an inert atmosphere to recover a fraction of higher-melting point, $\sim 31^{\circ}\text{C}$, (literature, $32-33^{\circ}\text{C}$). Samples were then melted into 15 mm pyrex tubes in an inert atmosphere and sealed under vacuum.

III. 3. Assignment of the Interactions.

Examination of $\text{Cl}_3\text{PNSO}_2\text{Cl}$ at -196°C between 20 and 40 MHz revealed eight interactions; two sets of four interactions each of equal intensity and together constituting four pairs whose respective frequencies are in the ratio of 1.2688, the reported¹² $\text{Cl}^{35}/\text{Cl}^{37}$ quadrupole moment ratio.

Since the frequencies of the Cl^{35}NQR , table 1, are so spaced and appear related as two pairs of interactions contrary to the molecular formulation implying three similar chlorines and one possibly unrelated, further investigation was felt warranted. Examination at higher temperatures revealed altogether only three pairs of interactions. To assist in the assignment of the observed interactions the Cl^{35}NQR spectra of some analogous compounds were considered. For the trichlorophosphazo group in $\text{Cl}_3\text{PNP}(\text{O})\text{Cl}_2$ and $[\text{Cl}_3\text{PNPCl}_3]^+$ the average frequency of the Cl^{35} interactions is 30.06 MHz¹³ and 30.0 MHz¹⁴ respectively. For some fifty compounds of the type RSO_2Cl the frequency of the Cl^{35} interactions of the chlorosulphonyl group ranges from 32 to 37 MHz¹⁴. Thus the highest frequency interaction observed in $\text{Cl}_3\text{PNSO}_2\text{Cl}$ is assigned to the chlorine bonded to the sulphur atom $\text{Cl}(\text{s})$ and the remaining three interactions to the phosphorus chlorines; $\text{Cl}(1)$, $\text{Cl}(2)$ and $\text{Cl}(3)$.

Table I

Cl^{35} NQR Frequencies of $\text{Cl}_3\text{PNSO}_2\text{Cl}$ at -196°C

P - Cl(1)	$30.132 \pm 0.0005 \text{ MHz}$
P - Cl(2)	$30.252 \pm 0.0005 \text{ MHz}$
P - Cl(3)	$31.783 \pm 0.0005 \text{ MHz}$
S - Cl	$32.715 \pm 0.0005 \text{ MHz}$

Unfortunately nothing is reported concerning the structure of the $\text{Cl}_3\text{PNSO}_2\text{Cl}$ molecule, almost certainly the P-N-S atomic skeleton will be reflected at an angle of about 120° , in which case one of the chlorines

bonded to phosphorus will be directed towards the $-SO_2Cl$ group, and hence its e.f.g. is affected by a polarization process, causing the considerably higher NQR frequency observed for Cl(3).

III. 4. Temperature Dependence of the NQR Frequencies

Over the limited temperature range studied below the onset of the phase transition, the temperature coefficients of the NQR frequencies are unusual. Three of the interactions have coefficients of approximately $-0.3 \text{ kHz deg}^{-1}$, which is extremely low for the chlorine nucleus that generally exhibits a variation of about -4 kHz deg^{-1} . Further Cl(2) has a coefficient of approximately $+0.2 \text{ kHz deg}^{-1}$. Above -184°C the coefficients become normal at -3 kHz deg^{-1} , although that of Cl(3) is about 10% greater, which can be related to its situation and interaction with the $-SO_2Cl$ group.

Positive NQR temperature coefficients have been reported for about seven inorganic molecules only but none of these is a molecular crystal. The normal negative temperature coefficient is the basis of the explanation of thermal averaging of the e.f.g. with increasing amplitude of lattice vibration or molecular motion. Reduction of $dp\pi$ bonding to a halogen-atom with increasing temperature will lead to an increase in its e.f.g., this process has been invoked¹⁵ to explain the positive temperature coefficients of most of these seven molecules. Thus it appears that in Cl_3PNSO_2Cl the $dp\pi$ bonding between the S and N atoms becomes reduced to zero above -191°C due to group reorientation vide infra. This delocalized charge is returned to the Cl_3PN - and $-SO_2Cl$ groups and hence partially to the Cl atoms.

III. 5. The Apparent Phase Transition.

The plot of the NQR frequencies versus temperature, (Figure 1), of the sulphur and phosphorus chlorines show a marked change in gradient and fall by 100 kHz and 30 kHz respectively between $-(191 \text{ and } 184)^{\circ}\text{C}$. This commences at approximately the same temperature of $-(190.8 \pm 0.2)^{\circ}\text{C}$ for all the interactions. In compounds of atoms of quadrupolar nuclei, phase transitions, whether order-disorder or displacive are plainly manifested in NQR frequency-temperature dependence plots, due to their extreme sensitivity to environment. Phase transitions can be inferred from plot discontinuity, abrupt frequency change or change in gradient.

The low melting point and high vapour pressure of $\text{Cl}_3\text{PNSO}_2\text{Cl}$ identifies it as a molecular crystal or geometrical array of molecules of minimal long-range forces. Thus direct intermolecular contributions to the e.f.g. will be virtually negligible. Since the abrupt change in gradient of the four plots of Figure 1 occurs at the same temperature the molecule as a whole is affected. Further the frequency readjustment is rapid and reversible, no hysteresis or inferred metastable phase is observed which together describe a continuous phase transition. This readjustment can originate from the effect of change in molecular geometry due to a change in the crystal packing which could be expected to exhibit an associated specific heat anomaly. Alternatively a variation in the very small non-bonded contribution to the e.f.g. can be responsible. A change in geometry would result in bonding or hybridization change and also of

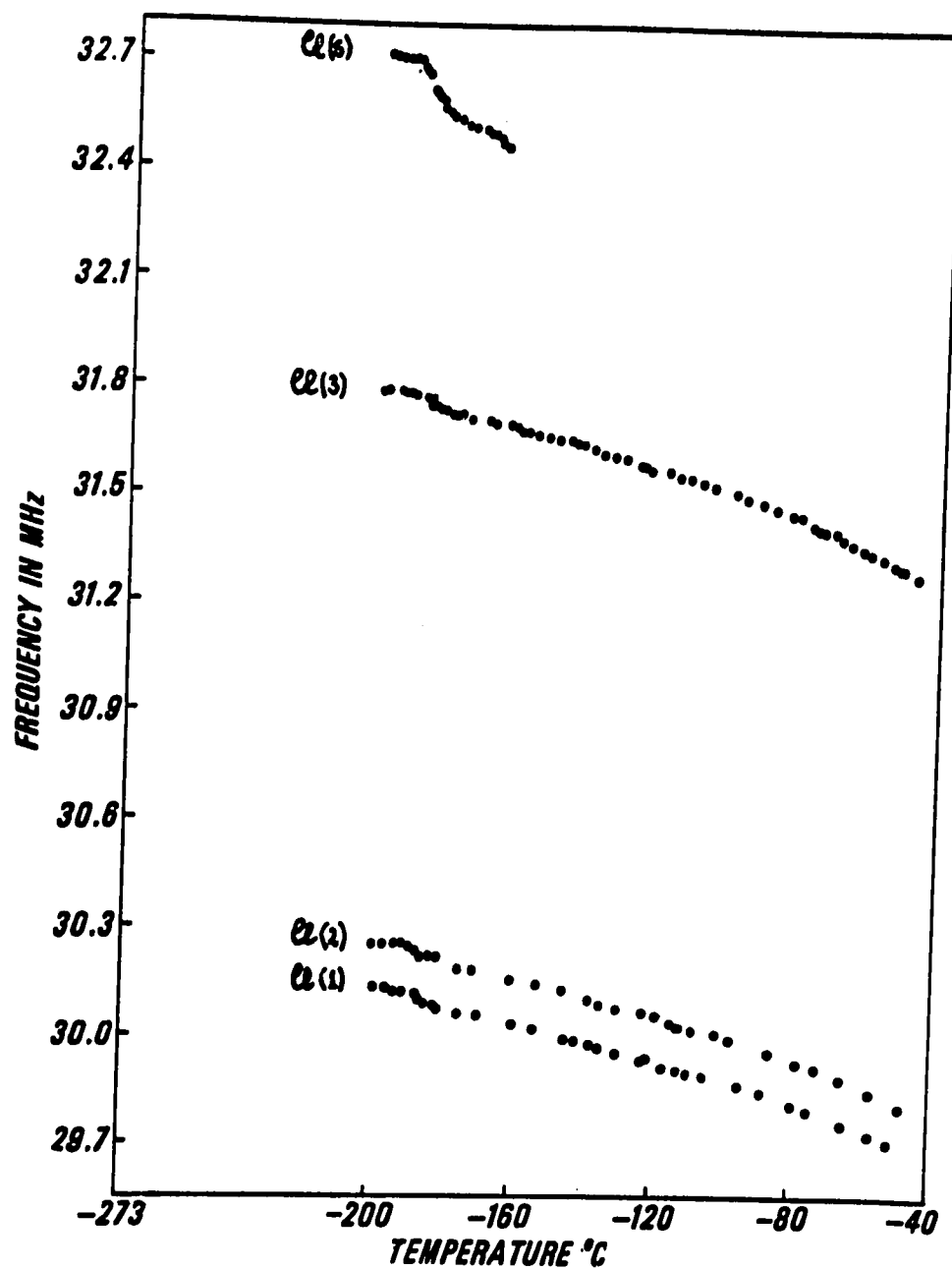


Figure 1.
 ^{35}Cl NQR Frequencies of $\text{Cl}_3\text{PNSO}_2\text{Cl}$
 versus Temperature.

the e.f.g. asymmetry parameter. Since the frequency readjustment is particularly small and also associated with a change of temperature dependence, the semi-rigid molecule's NQR frequencies are little affected but the characteristic of its torsional oscillations are very considerably. These must change greatly across the phase transition. It seems reasonable to describe this observation as a displacive phase transition, that would arise from the effect of interactions between torsional and centre of gravity lattice modes on molecular reorientation¹⁶. Thus there results a change in the phonon flux which would only have a minor entropic and hence associated calorimetric factor. Unfortunately due to the low temperature of this transition and the extreme reactivity of the compound, calorimetric investigation is not presently considered practical. It is to be noted that these observations are at constant pressure and not constant volume.

The line-width data of the phase transition region provide further information of the processes occurring. The line-width of the sulphur-chlorine interaction, (Figure 2), is constant with increasing temperature until about -192°C when rapid broadening occurs to a maximum value of 36 kHz at $-(191.2 \pm 0.2)^{\circ}\text{C}$ before falling back to 22 kHz at -191°C and then a slow increase occurs to a maximum value of 36 kHz at about -169°C . The line-width data of the phosphorus-chlorine interaction studied is quite different, (Figure 3), it is constant with increasing temperature until about -190°C when a slow broadening commences to 23 kHz at $-(184.0 \pm 0.5)^{\circ}\text{C}$ before falling back to a constant value. It is at

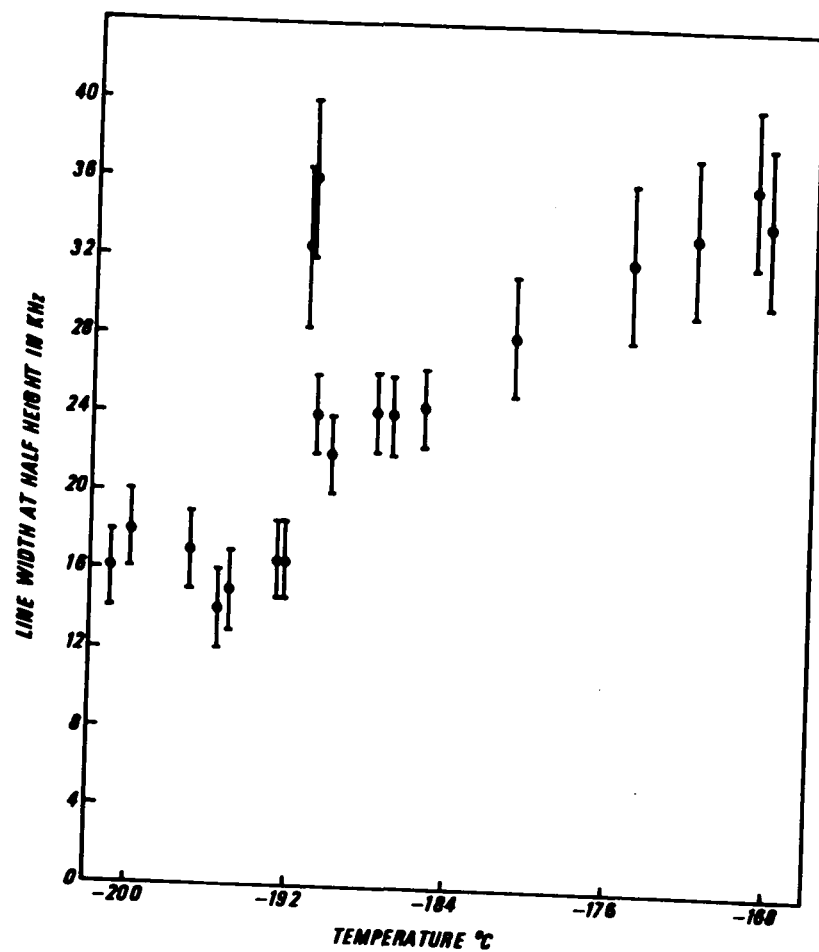


Figure 2.

Cl(S) NQR Line-width versus Temperature.

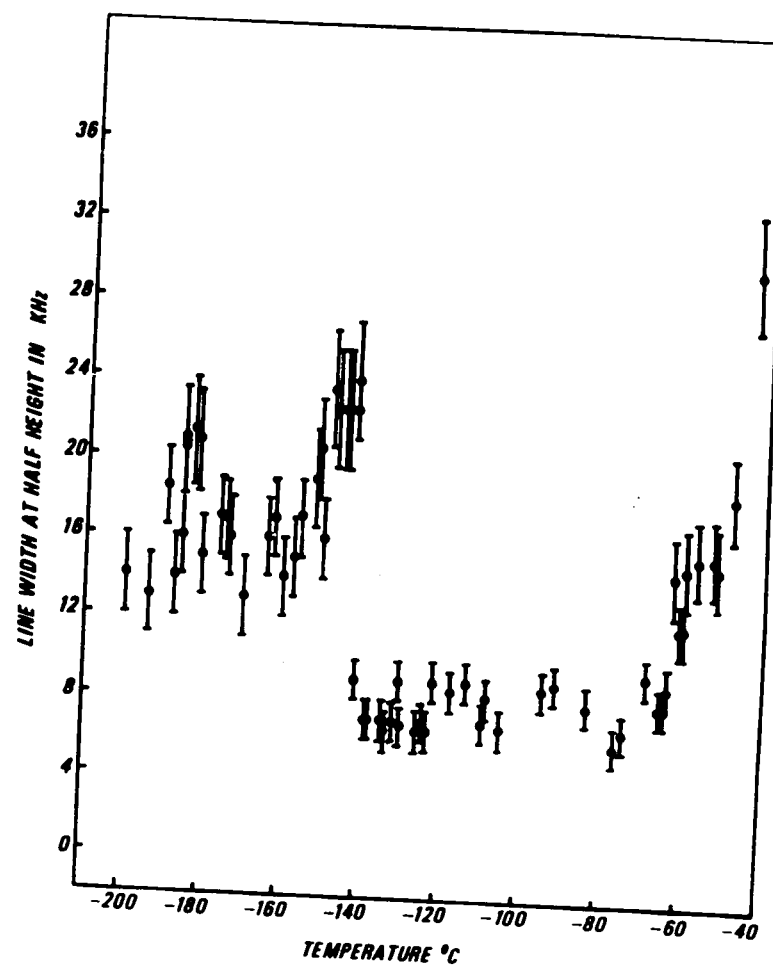


Figure 3.

Cl(3) NQR Line-width versus Temperature.

about -184°C that the temperature coefficient of the NQR frequency appears to attain a maximum value and thus this is the temperature when the phase transitional process, which commenced at -192°C , is considered to be most effective.

It is significant that above and below the phase transition temperature the line-width returns to the same constant value. A major change in molecular geometry or a first-order phase transition would be expected to lead to variation of the dipolar contributions to the line-width. This observation is regarded as further evidence against its recognition as such a phase transition.

The data of the phosphorus-chlorine interaction studied is considered representative of the behaviour of all the phosphorus chlorines for which periodic checks were made confirming this. The interactions were far more frequently observed than were line-width data taken, particular attention was paid to the phosphorus-chlorine interaction in the lower temperature region where the sulphur-chlorine interaction exhibits rapid broadening, vide infra.

An extensive NQR study of phase transitions in malonitrile has been reported¹⁶. Considerable line broadening is observed at the phase transitions and attributed to extremely rapid critical fluctuations that are considered diagonal, having no appreciable effect on the e.f.g. Additionally the transitions are observed to have no effect on the spin-lattice relaxation time. Thus the observed broadening occurring about -184°C and which subsequently becomes reduced, is not attributed to life-

time broadening but is interpreted as being due to the production of disorder by the incipient molecular motion. Only an investigation by pulse methods could clarify this point.

The observed maximum line-width at $-(184 \pm 0.5)^{\circ}\text{C}$ is not due to life-time broadening but to lattice disorder caused by the phase transition¹⁶. The extremely rapid broadening of Cl(S) line-width at $-(191 \pm 1)^{\circ}\text{C}$ is at six degrees below the broadening of the Cl(1), Cl(2) and Cl(3) lines, and is interpreted as evidence that the Cl(S) and the Cl(1), Cl(2) and Cl(3) are involved in different processes.

III. 6. Interpretation of Spectral Broadening.

After the recovery from the maximum in the line-width of the sulphur-chlorine interaction at $-(191.2 \pm 0.2)^{\circ}\text{C}$, the interaction broadens progressively with increasing temperature until non-observation at above -168.3°C . NQR spectral broadening over such a temperature range is very typical of life-time broadening. Application of equation 1 of Chapter I, §4, to the data of Figure 2 yields a value of $(940 \pm 60) \text{ cal mol}^{-1}$ for the hindering potential. It seems reasonable to attribute this broadening to the onset of some hindered reorientational motion of the $-\text{SO}_2\text{Cl}$ group about the N-S bond. The potential barrier would result from neighbouring group interactions and to a greater extent from the intramolecular bonding and steric effects as discussed earlier and thus would be unpredictably many-fold and would destroy $\text{dp}\pi$ bonding. Investigation of reorientation about the N-S bond has been reported¹⁷ in a sulphinamide in solution and recognized to be extremely rapid with an activation energy of $8.1 \text{ kcal mol}^{-1}$.

and a frequency factor of $2.4 \times 10^9 \text{ sec}^{-1}$. Similar investigation of the N-S bond in sulfenamides in solution has indicated a higher barrier to rotation with activation energies of $(14.5 \pm 2.5) \text{ kcal mol}^{-1}$ for various compounds¹⁸.

The rapid increase in line-width with decreasing NQR frequency of Cl(S) is quantitatively similar to the initial line-width behaviour of 1,2-dichloroethane¹⁹ which passes through a maximum during a transition over which there is 13 per cent reduction in the Cl^{35} NQR frequency. However, the 1,2-dichloroethane interaction is observable above this transition, which is interpreted as due to the onset of re-orientational motion about the principal inertial axis of the molecule that is inclined at 19.16° to the principal axis of the e.f.g. tensor. Application of equation 2 approximately accounts for this observation in 1,2-dichloroethane. Application of equation 2 of Chapter I, §4, for free rotation of the $-\text{SO}_2\text{Cl}$ group about the N-S axis would average the e.f.g. at the chlorine nucleus by a factor of 2/3, from that of the quasi static molecule, assuming a tetrahedral configuration for the group. Such an averaged frequency was not detected in a search over an extensive frequency range at -80°C .

From -140°C the line-width is constant with increasing temperature until about -70°C when broadening commences and is observed to attain a maximum value at -46.3°C , (Figure 3). All three interactions are similarly affected and are unobservable above this temperature when the sample appears to change from white to translucent. Over the next eighty-eight degrees, to the melting point of the compound, no quadrupolar interactions are observable. Application of equation 1 for life-

time broadening, to the data of Figure 3, yields a value of (6.3 ± 0.3) kcal mol⁻¹ for the hindering potential of the reorientation of the Cl₃P- group about the P-N axis. This agrees well with the reorientational barrier of 12 kcal mol⁻¹ about the P-N bond, reported²⁰ for C₆H₅P(Cl)N(CH₃)₂ from the proton nuclear magnetic resonance spectrum in solution, that coalesces at $-(50 \pm 2)^{\circ}\text{C}$. In this molecule lone-pair-lone-pair interaction would also contribute to the barrier.

III. 7. Discussion of the Line-width.

The line-widths of both the sulphur and phosphorus chlorines are the same in the low temperature region. This is surprising, for a considerable portion of the line-width must result from the sum of various different dipolar contributions (and probably only from within the molecule) which can only coincidentally be identical for the chlorines of both the -SO₂Cl and Cl₃P- groups, thus indicating the importance of other contributions. Except in the temperature region of onset of motional processes and disorder effects, the line-widths of the interactions, (Figure 3), are constant at $(16.0 \pm 0.5)\text{kHz}$ below $-(145 \pm 1)^{\circ}\text{C}$ and $(8.0 \pm 0.5)\text{kHz}$ above this temperature. That the constant low temperature line-width is reduced by a factor of two to a further constant value at higher temperatures is interesting. To account for the former condition, postulation of a large static or electrical broadening contribution to the line-width is necessary, that then becomes absent or greatly reduced at higher temperatures. Conversely and speculatively it could be postulated that a dominant low temperature relaxation mechanism might become ineffective at higher temperatures. It is known that the spin-spin contribution of the line-

width to a certain extent reflects the thermal history of the sample, but since this reduction is reversible and always over the same temperature, it is not considered responsible. The experimental $B+$ was varied and had no immediate effect on the line-width, thus excluding the possibility of it being the result of saturation of the nuclear spin system. If the $-SO_2Cl$ group is undergoing rapid or complete reorientation then its dipolar contribution to the line-width would become averaged to zero. Such a process might account for some of the apparent reduction in line-width with increasing temperature. Clearly direct measurement of relaxation time parameters is necessary before any explanation of the observations can be provided.

The behaviour of the line-width about $-(145 \pm 1)^\circ C$ is interesting. The recorded interaction passes through an intensity minimum and is observed to reverse phase by 180° over a two-degree temperature range, however the temperature dependence of the NQR frequency appears unaffected. Effort was made to establish that this signal phase change is not an instrumental effect from detecting the narrower interaction, further it was observable when the temperature is cycled in either direction. The line-width maximum at $-(145 \pm 1)^\circ C$ in Figure 2 has no significance and is the result of line-width definition of a rather complex recorded interaction at the transitional temperature. No explanation of this observation can be offered and due to the complexity of detection of mixed mode signals by s.r. oscillators along with phase sensitive detection, it is improper although tempting, to assert that it might reflect detection of an interaction of more dispersive than absorption components, or vice-versa.

It is interesting to again consider the $-\text{SO}_2\text{Cl}$ group interaction which is undetectable above $-(168.3)^\circ\text{C}$, some twenty-three degrees below this line-width anomaly. This rapidly reorienting group will generate a time varying dipolar magnetic field which would modulate the surrounding quadrupolar nuclei and hence have a critical effect on their line-widths through affecting the life-times of their excited states. Possibly this activity becomes critical at $-(145 \pm 1)^\circ\text{C}$ and it is at least consistent with there being no associated NQR frequency temperature dependence anomaly. Furthermore it could also account for the associated observed interaction intensity minimum through its effect on the transition probabilities.

III. 8. Summary

On the basis of the Cl^{35} NQR frequencies for the $-\text{PCl}_3$ and $-\text{SO}_2\text{Cl}$ groups in other molecules it is possible to assign the high frequency line in $\text{Cl}_3\text{PNSO}_2\text{Cl}$ to the $-\text{SO}_2\text{Cl}$ group, and the three lower frequency lines to the $-\text{PCl}_3$ group. One of the lines of the $-\text{PCl}_3$ group is at a higher frequency due to the $\text{Cl}(3)$ proximity to the $-\text{SO}_2\text{Cl}$ group. The relative intensities of the four lines support this assignment, as does their temperature dependence and their respective line-width behaviour.

With this assignement it is possible to interpret the line broadening as due to the behaviour of the groups. Reorientational motion leads to life-time broadening that gives an energy barrier of $(940 \pm 60) \text{ cal mol}^{-1}$ for $-\text{SO}_2\text{Cl}$ group and $(6.3 \pm 0.3) \text{ kcal mol}^{-1}$ for $-\text{PCl}_3$ group. The broadening behaviour supports the assignment.

Frequency and line-width temperature dependence together indicate a phase transition at $-(184.0 \pm 0.5)^\circ\text{C}$.

Additional features of the spectrum remain to be explained; the line-widths are large and equal for all four lines at low temperatures, the three lines of $-\text{PCl}_3$ have half this line-width at higher temperatures, and the detected signal changes phase at $-(145 \pm 1)^\circ\text{C}$. Further explanation requires a precise knowledge of the molecular structure and a detailed study of the parameters of the various inherent relaxational processes.

Chapter III

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CHAPTER IV

Temperature Dependence of the Chlorine-35 Nuclear Quadrupole Resonance Spectrum of the Trimethylamine Borontrichloride Complex.

IV. 1. Introduction.

The complex of trimethylamine and borontrichloride is one of a series of related molecules that has been the subject of a wide-line magnetic resonance study¹. The proton line-width have been observed as a function of temperature in this molecule, their second moments interpreted in terms of molecular motions and the activation energies determined. The molecular symmetry and boron-chlorine bonds afford an excellent opportunity for further investigation of the solid.

Since molecular torsional transitions occur often on a nuclear time scale but even less rapidly than the torsional oscillations, the nucleus experiences an average over the torsional energy levels, of an average e.f.g. associated with each torsional state. Thus there is a reduction in the NQR frequency from that expected for the static lattice. The concept of the amplitudes of all these motions being temperature dependent is the basis of the explanation of the normally observed temperature dependence of the NQR frequency. Onset of additional lattice or molecular motion, at a sufficient frequency to effect e.f.g. averaging, will result in a minor variation in the temperature dependence of the NQR frequency. Thus new vibrational modes will always be associated with and might even result in second-order phase transitions, particularly as evident from NQR temperature dependence studies.

While solid-solid phase transitions are associated with changes in molecular rotational freedom, they need not involve major reordering of the crystal lattice or even have associated specific heat anomalies. Nevertheless they are plainly manifested by line-width in addition to temperature dependent quadrupole coupling data. Since magnetic and quadrupole resonance line-widths usually have a considerable magnetic dipolar contribution, onset of group or molecular reorientational motions affect the magnitude of this experimental parameter. Of more significance in NQR spectra are the relaxation effects that lead to line-broadening. Slow group or molecular torsional oscillations may occur at or have frequency components comparable to the NQR precessional frequency and will then lead to life-time broadening. Also motions such as random and large angle reorientations from neighbouring molecules will modulate the e.f.g. of the resonant nuclei. These fluctuations can induce transitions between quadrupolar energy levels, thus to rapid relaxation and hence line-broadening. Finally but of less significance here, randomization of the e.f.g. due to disorder, electrical strains and thermal gradients all contribute to line-broadening.

IV. 2. Experimental⁹

The sample was prepared by the standard method², vacuum sublimated to yield transparent crystals, handled under dry nitrogen, ground to a white but still visibly crystalline powder and sealed in pyrex tubing under vacuum. The sample, contained in a copper cavity,

was positioned in or over liquid nitrogen or slushes for temperature control. This was determined from thermocouple data, one junction being attached to the sample tube. Care was taken to exclude the effects of a thermal gradient over the sample. The terrestrial magnetic field was ignored.

The weak NQR interactions after phase-sensitive detection were displayed with a strip-chart recorder, the line-width being taken as their full width at half-height and determined on a precalibrated scale. Super-regenerative oscillators are considered to yield only distorted line shapes, nevertheless through operation at standardized conditions with the aid of a spectrum analyzer and at minimal level of modulation, the observed line-widths were considered representative and minor instrumental effects, if present, constant. Thus these line-widths are described as "apparent".

IV.3. Results.

The frequencies of both the Cl^{35} NQR interactions of the trimethylamine borontrichloride complex above 77°K are plotted in Figure 1. Both interactions exhibit a normal frequency diminution with increasing temperature. The respective plots are not smooth but each exhibits an obvious change in gradient at $(201 \pm 1)^\circ\text{K}$ and another but less pronounced change at $(100 \pm 2)^\circ\text{K}$. This latter change is less obvious, for at that temperature the line-widths of the recorded interactions are very broad, thus introducing considerable imprecision into the frequency determination.

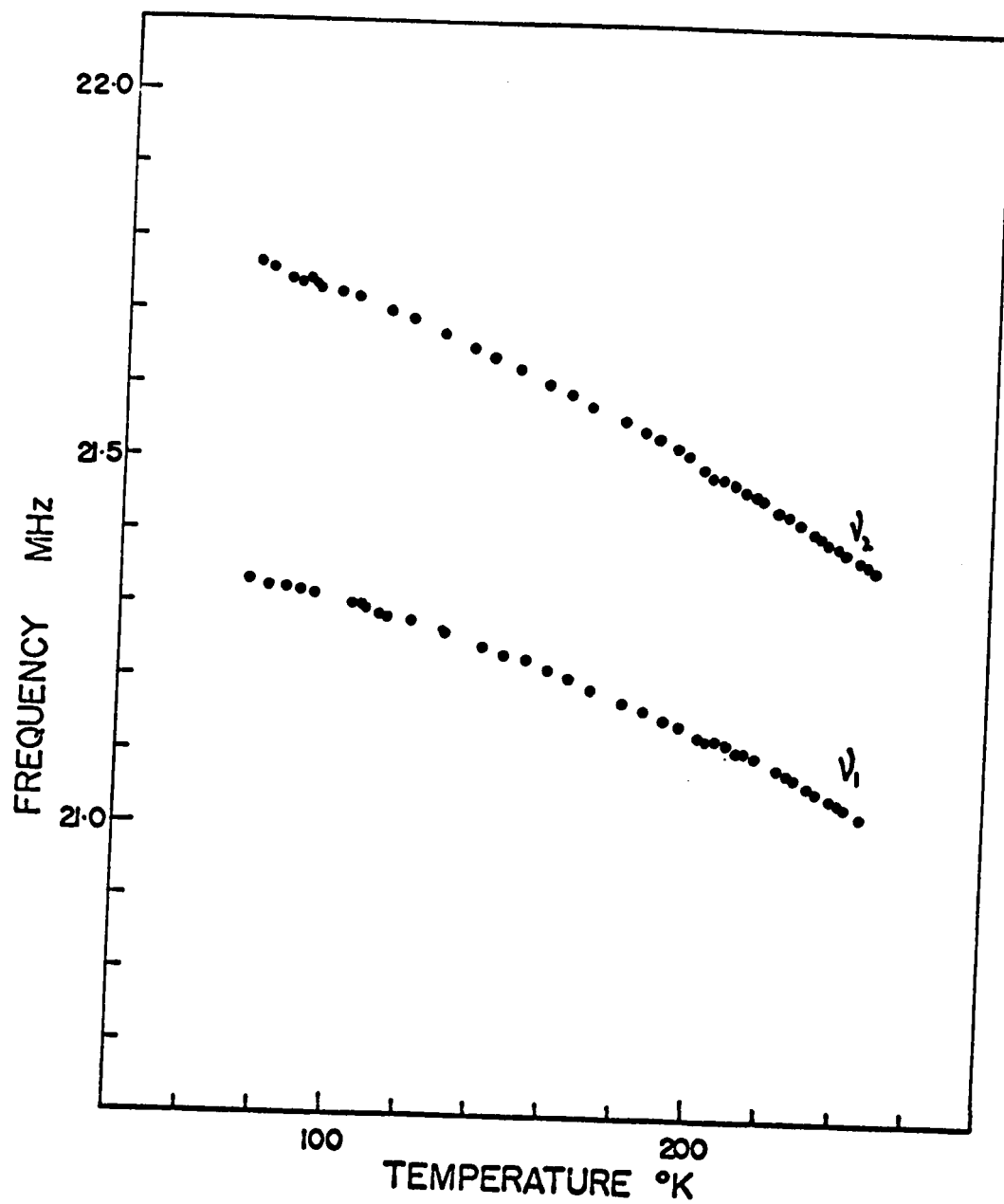


Figure 1.

Plot of the ^{35}Cl NQR frequencies of the trimethylamine-borontrichloride complex versus temperature.

The plot of the stronger interaction apparent line-width at half-height, versus temperature, is shown as a continuous line in Figure 2. Both interactions exhibited broadening between 80 and 120°K, with a maximum about 100°K, the temperature of first gradient change in the NQR frequency versus temperature plot. The line-width is narrow and approximately constant until about 235°K when rapid broadening commences until $(247 \pm 2)^{\circ}\text{K}$ the temperature above which the interaction are unobservable.

IV. 4. Treatment of the Temperature Dependent Frequency Data.

The NQR data above 77°K was treated by least squares fitting to a curve developed from the Bayer³, Kushida⁴ and Brown⁵ NQR temperature dependence theory, using the McGill I.B.M 360/75 machine. The effect of a finite asymmetry parameter was ignored. The results of two treatments of the data are listed in Table 1. The data points of both interactions were fitted to their respective single curves, also the data sets were separated at 200°K, which as can be seen in Figure 1, is the temperature of their pronounced change in gradient. It was considered impractical to further separate the sets at the temperature of the less pronounced gradient change evident in the vicinity of 100°K, due to the resulting lower temperature data set that would be too small for valid application of the fitting procedure. The root-mean-square deviation of the separated curves are improved over that of each complete data set, thus the separation is justified and the apparent change of gradient at 201°K confirmed. It can be regarded as a phase transition.

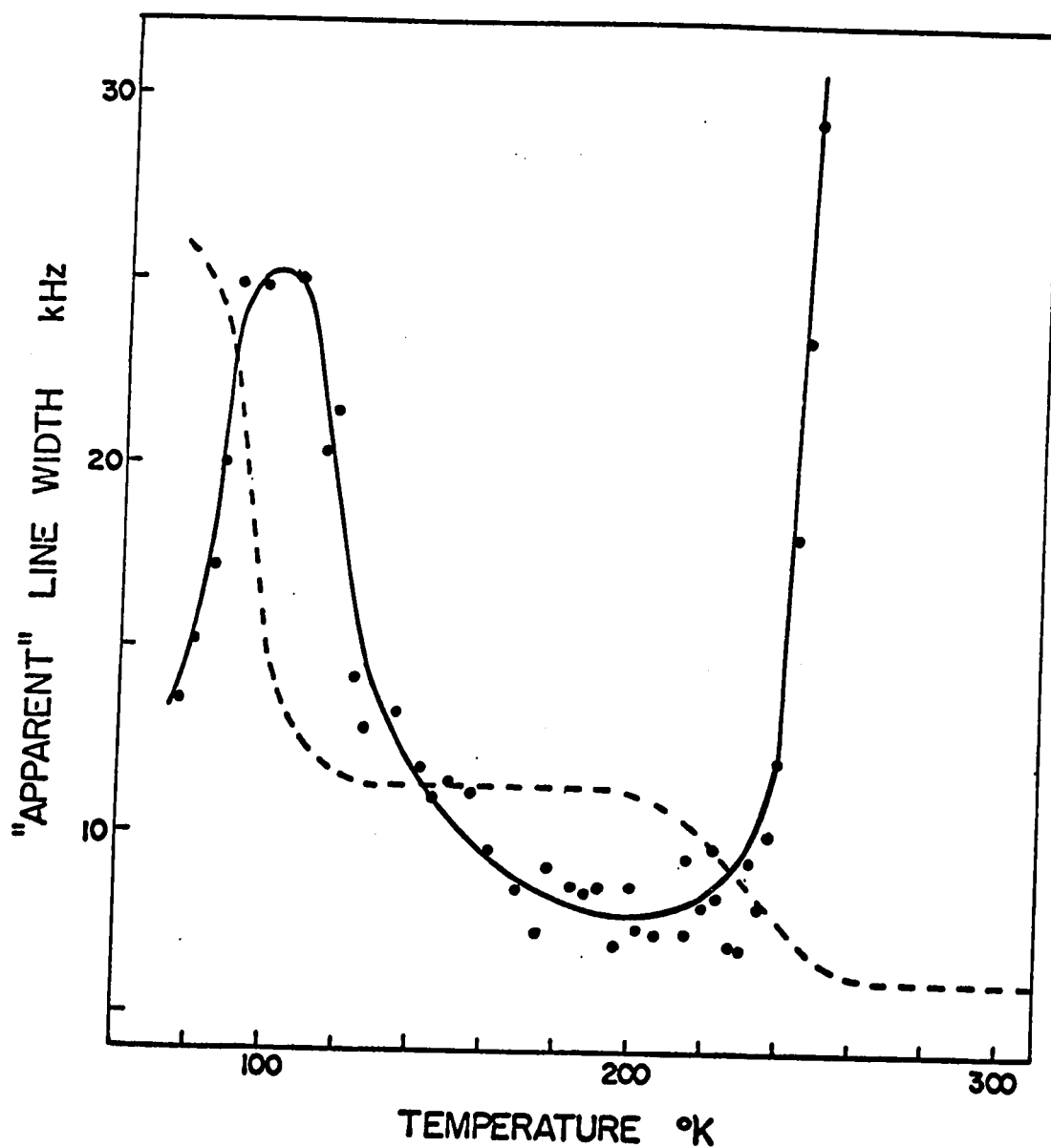


Figure 2.

Plot of the apparent line-width at half-height of the stronger ^{35}Cl interaction of the complex versus temperature—continuous line. The proton second moment from reference 1 is plotted on the same temperature scale but with an arbitrary ordinate scale—dotted line.

All the least squares Bayer-Kushida-Brown curve fits were performed on molecular models with two different moments of inertia. In view of the cylindrical shape of the molecule, torsion about the molecular axis only was considered. A moment of inertia of 5.9267×10^{-38} gm cm² was calculated from the room temperature structural data⁶ for the model of the BCl₃ group undergoing torsion against the remainder of the molecule rigidly fixed. Similarly the model of the molecule oscillating as a rigid body has a moment of inertia of 7.4264×10^{-38} gm cm². In both models the methyl groups were considered as fixed masses. It might be expected that the appropriateness of either model for a particular temperature range would be reflected in its respective root-mean-square deviation, this expectation is not clearly borne out.

IV. 5. Discussion.

The line-width changes can be compared with the proton second moment transitions derived from observation of the molecule¹ and their coincidence is evident in Figure 2. Thus it seems reasonable to relate the broadening about 100°K to the inferred onset of reorientation of the methyl groups and not to the effects of lattice disorder. About this temperature their torsional frequencies or Fourier components must approximate the Cl³⁵ nuclear precessional frequencies which would result in a very effective relaxation process and hence life-time broadening. At higher temperature the reorientational rate must increase beyond effectiveness and a normal line-width is regained.

TABLE 1

Results of Fitting the NQR Data in the Bayer-Kushida-
Brown Temperature Dependence Curve

Assignment	Moment of Inertia $\text{gm cm}^{-2} \times 10^{-38}$	Vibrational Frequency cm^{-1}	Alpha $\text{deg}^{-1} \times 10^{-4}$	Resonance Frequency in MHz Rigid Lattice, at 0°K	Root-mean-square Deviation Hz
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All data points:

ν_1	5.9267	65	9.1	21.435	21.387	2474
ν_1	7.4264	59	9.2	21.433	21.391	2464
ν_2	5.9267	58	8.9	21.885	21.832	3156
ν_2	7.4264	52	8.0	21.883	21.835	3166

Data between 77 and 200°K :

ν_1	5.9267	66	9.8	21.434	21.388	2018
ν_1	7.4264	60	10.0	21.431	21.390	2011
ν_2	5.9267	60	9.7	21.880	21.828	3128
ν_2	7.4264	54	9.9	21.877	21.830	3130

Data above 200°K :

ν_1	5.9267	119	19.6	21.300	21.274	1874
ν_1	7.4264	106	19.6	29.299	21.276	1873
ν_2	5.9267	65	10.7	21.831	21.784	2582
ν_2	7.4264	58	10.7	21.830	21.787	2581

The phase transition at $(201 \pm 1)^{\circ}\text{K}$ has no obvious associated line-broadening, but since there is a change in the temperature dependence of the NQR frequency, a slight reordering of the lattice leading to either abrupt amplitude increase or inclusion of additional modes of lattice vibrational freedom must be involved.

Above 200°K a proton second moment transition is observed to commence, Figure 2. About its maximum, the line-width exhibits rapid broadening until it becomes unobservable at $(247 \pm 2)^{\circ}\text{K}$. This transition has been associated with onset of hindered rotation of the molecule as a whole around the B-N internuclear axis¹. Again the observed broadening can be attributed to direct relaxation effects through a life-time limiting process. About 247°K the jump rate of the thermally activated hindered reorientational motion must approach the Larmor frequency.

Above $(247 \pm 2)^{\circ}\text{K}$ the interactions are no longer observable. If it is assumed that the frequency of the inferred reorientational motion of the BCl_3 group around its figure axis is uniform and in excess of the nuclear precessional frequency, then the e.f.g. at the chlorine sites would be averaged around this axis to $1/3$ of its original value. This is the value of $0.5(3 \cos^2 \theta - 1)$, where θ denotes the angle between any B-Cl bond axis, (i.e., the principal direction of the e.f.g. tensor at the chlorine site in the previously static group), and the principal inertial axis of the molecule. Effort was made to detect an average NQR frequency at higher temperatures, without success. If this prediction is correct then the non-observation might be rationalized against the feebleness of the interactions,

even prior to the line broadening and also by the Bohr-Einstein relationship of frequency to energy.

It is to be noted that although the room-temperature X-ray structural analysis of this molecule distributed the chlorines between two sites, this is not incompatible with the above rationalization of the line-broadening by postulation of hindered molecular reorientation. The time-scale of the X-ray observation is very much shorter than for the NQR and also sufficiently rapid to locate atoms confined to potential wells whilst executing hindered reorientation.

It is not considered worthwhile to attempt to estimate the potential energy of the inferred barrier about 247°K by application of equation 2 of Chapter I.4, to the apparent line-width data. The observed broadening of the weak interaction is very rapid just below this temperature introducing considerable indeterminacy into the line-width measurement.

Both the solid-state proton magnetic resonance and NQR spectra of 1,2-dichloroethane have been studied⁷. It is known to exhibit a specific heat maximum about 170°K , to undergo lattice expansion and the molecule is inferred from diffraction studies to be fixed below and rotating above this temperature. The proton second moment exhibits a transition between 165 to 180°K , above this temperature the proton line-width decrease corresponds to full intramolecular narrowing from 360° motion about an axis perpendicular to that connecting adjacent protons. Over the same temperature range the Cl^{35} NQR is also broadened

and shifted to lower frequency. The frequency shift is accounted for by the high temperature phase diffraction study that revealed full 360° reorientation at greater than 10^6 Hz, about an axis through the two chlorine sites and that is nearly coincident with the principal inertial axis. Calculations however fail to predict the observed amount of Cl^{35} line-broadening ⁸.

IV. 6. Conclusion.

The behaviour of the proton second moment and Cl^{35} NQR spectra of the trimethylamine borontrichloride complex is similar to that of the only other molecule in the literature with comparable data, 1,2-dichloroethane that is however better understood. The similarity supports the interpretation of the results of the complex in terms of reorientational motion. The coincidence of the proton second moment transitions and the Cl^{35} NQR line-broadenings at the same temperatures strongly suggests that each respective set is due to the same thermally activated process.

The NQR spectrum is in agreement with the room temperature X-ray structural analysis. In the region of the low temperature proton second moment transition at about 100°K , a phase transition is suspected. Prior to the onset of the high temperature transition at about 201°K another is confirmed. Considerable information is provided in support of the interpretation of the proton magnetic resonance study however there is only additional but no positive evidence for full reorientational motion of the BCl_3 group.

The rationalization of the line broadening processes by direct relaxation is speculative and could be confirmed in a steady-state experiment by observation of the much weaker Cl^{37} NQR spectrum. This should also exhibit broadening, but displaced to a slightly lower temperature, to an extent proportional to the magnetogyric ratios of the chlorine quadrupolar isotopes.

Chapter IV

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CHAPTER V.

CHLORINE NUCLEAR QUADRUPOLE RESONANCE STUDY OF SOME PHOSPHORUS - CHLORINE COMPOUNDS

V.1. Interpretation of the Stereochemistry of the Solid Phenylchloro- phosphoranes from their Chlorine NQR Spectra:

Table 1: Chlorine NQR Frequencies of two Phenylchlorophosphoranes at 77°K

	Cl^{35}	Cl^{37}
Phenyltetrachlorophosphorane, Ph PCl_4 :	33.583 + 33.741 +	26.469 26.593
Diphenyltrichlorophosphorane, Ph_2PCl_3 :	33.452	26.366

+ each interaction of equal intensity, reference 1.

It would be useful to rationalize the observed NQR spectra of the phenylchlorophosphoranes against respective molecular structures in the absence of any solid-state structural information. The following information has been established, through various spectroscopic techniques, for the trigonal-bipyramidal stereochemical model invariably recognized for the penta-coordinated phosphorus ($\bar{\text{V}}$) atom²: Cl^{35} NQR frequencies in the molecular compounds $\text{A}_{5-n}\text{P Cl}_n$, where A is strictly alkyl, aryl or halogen, are observed in excess of 29 MHz³; in such molecular compounds, axial (apical) chlorines exhibit a Cl^{35} NQR frequency about 29.2 MHz; equatorial chlorines, about 33.7 MHz⁴; and bulky groups or the relatively less electronegative substituents adopt a preferred equatorial stereochemical orientation⁵.

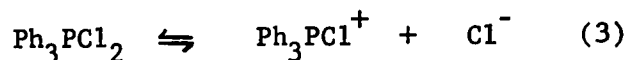
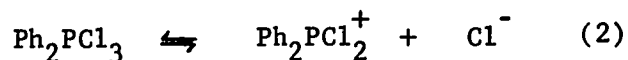
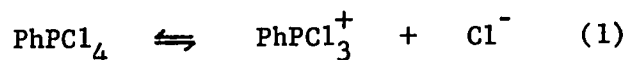
An attempt to explain the Cl^{35} NQR spectrum of phenyltetrachlorophosphorane observed at an average frequency of 33.66 MHz, in terms of a possible molecular structure, in accordance with this information, proved impossible¹. Instead of a trigonalbipyramidal conformation, an alternative molecular structure with four equivalent chlorines is suggested.

The observation of the single interaction of diphenyltrichlorophosphorane at 33.452 MHz is also irreconcilable on a trigonal-bipyramidal molecular model. This would require two Cl^{35} interactions in the intensity ratio 1 to 2, or 2 to 1 with respect to the frequencies 29.2 and 33.7 MHz, or even a single interaction at 29.2 MHz, depending on the positions of the phenyl groups about the phosphorus atom. Clearly the Cl^{35} NQR spectra observed for the two phenylchlorophosphoranes at 77°K is at variance with the trigonalbipyramidal stereochemistry recognized for their congeners. It can be added that the likelihood of occurrence of intramolecular exchange, (Berry rotation⁶), which has been held responsible for the observed averaging of the fluorine magnetic environments with retention of spin-coupling in similar compounds⁷, would be an implausible explanation for these observations from the solid-state.

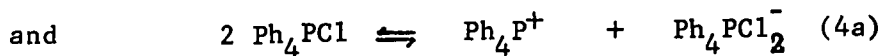
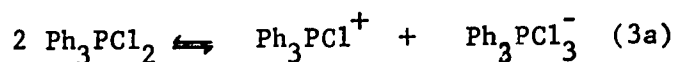
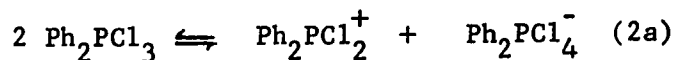
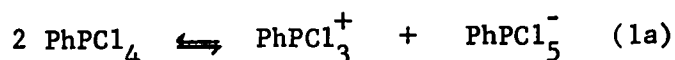
The phosphoruspentachloride molecule has long been a known⁸ to exist in the solid-state as the tetrachlorophosphonium and hexachlorophosphate ions that are responsible for its normally observed chlorine NQR spectrum. Nevertheless after low pressure vacuum sublimation of a sample it was possible to observe the chlorine NQR spectrum of molecular PCl_5 ⁴. Further it is known that the molecular forms of halophosphoranes undergo slow transformation to solid modifications at room-temperature⁹. Conductance studies of

the phenoxyhalophosphoranes in ionizing solvents indicate their existence therein as the polyhalopolyphenoxyphosphonium and the polyhalopolyphenoxyphosphate ions¹⁰. The trifluoropolyhalophosphate and mixed hexahalophosphate ions are similarly known¹¹.

Considering these observations it is not unreasonable to suggest ionic forms for the solid phenylchlorophosphoranes arising in the following manner:



The probable species present in the solid will be dictated by the relative ease of the breaking of the various bonds. The above possibilities are considered preferable to the following:



The phosphate anion is rejected in preference for the simple chloride ion as intramolecular steric interactions resulting from crowding would limit its stability. The many other possible schemes are all unsatisfactory as they would require rupture of the P-Ph linkage.

It is now pertinent to consider the NQR spectrum of the tetrachlorophosphonium ion, PCl_4^+ , that contains Cl^{35} interactions at an average frequency of about 32.4 MHz, and that of the hexachlorophosphate ion, PCl_6^- , averaging 29.5 MHz. The Cl^{35} NQR frequencies of both phenylchlorophosphorane compounds are close to that of the cation, an observation that favours schemes 1 and 2 over 1a and 2a respectively. There is no obvious explanation for these being one megahertz higher than that of PCl_4^+ , contrary to that to be expected from replacement of chlorines, presumed to have a greater inductive effect, by phenyl groups, being lesser in this respect. A similar apparent frequency reversal is demonstrated by the chlorofluorophosphorane series including phosphoruspentachloride and also the chlorophosphine series that exhibit a Cl^{35} NQR frequency increase on replacement of the fluorine atom by chlorine³, that is regarded to be less inductive on the basis of atomic electronegativity considerations. The proximity of the frequencies of the inferred cations PhPCl_3^+ and $\text{Ph}_2\text{PCl}_2^+$ is a further example of apparent insensitivity already recognized as being demonstrated by the RPOCl_2 system in which the phosphorus atom fails to transmit or buffers inductive effects of varying R, unlike the carbon atom¹².

In the absence of X-ray structural analysis, this interpretation of the observed Cl^{35} NQR spectra of the phenylchlorophosphoranes in terms of the preferred ionic formulations can only be regarded as tentative. The existence of the first chlorophosphonium ion excepting the tetrachlorophosphonium ion has recently been reported. An X-ray structural determination of the product of the reaction between chlorotriphenylphosphinegold and cis-bis(trifluoromethyl) -1,2-dithietene indicated the presence of the triphenylphosphonium cation¹³. ³¹P nuclear magnetic resonance studies are unlikely to yield additional

information considering the small chemical shifts and broad lines exhibited by this nucleus in the solid-state. Differential thermal analysis measurements have demonstrated the ionization transition in phosphoruspentachloride⁴. Dielectric measurements have been employed in the study of the low-temperature molecular structure of PClF_4 ¹⁴. Vibrational spectral studies hold promise for the structural determination of these molecules, however there still appears in the literature difference of opinion on assignment and also interpretation of the correct molecular symmetry of the compounds of the $\text{PCl}_n\text{F}_{5-n}$ series¹⁴. The interpretation of the vibrational spectrum of methyltetrachlorophosphorane¹⁵ in non-ionizing solvents is in terms of a monomeric unit, and in the solid-state, an ionic formulation, $\text{MePCl}_3^+ \text{Cl}^-$. This is exactly in analogy with scheme 1 inferred for phenyltetrachlorophosphorane.

A sample of tetraphenylchlorophosphorane was examined over the frequency range 6 to 35 MHz and no quadrupolar interactions were detected, a result predicted by scheme 4. No sample of triphenyldichlorophosphorane was available for study. Under solvation it is understood to dissociate¹⁶ by scheme 3 and evidence is presented to rule out the formulation of scheme 4a. It may be possible to observe also the NQR spectra of the molecular forms of these compounds at higher temperature, when they are just prepared or after sublimation at low-temperatures. At room-temperature the samples employed exhibited no quadrupolar interactions and above 77°K their weak interactions soon lost intensity and appeared normal in continuity and temperature dependence.

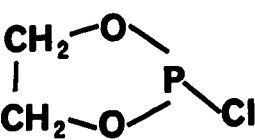
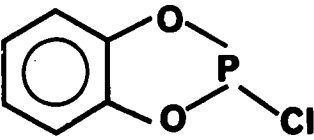
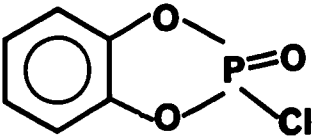
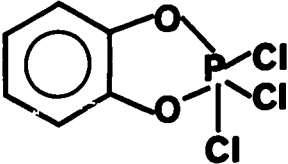
V.2. Discussion of the Chlorine-35 NQR Spectra of Some Cyclic Phosphorus Esters:

The only X-ray structural determinations of molecules containing the penta-coordinate phosphorus atom with halogen substituents are those of the N-methyltrichlorophosphinimine dimer^{17,18}, $(\text{Cl}_3\text{PNMe})_2$, and of its mono-phenyl derivative¹⁹. These confirm what is already well known from microwave studies of penta-coordinate molecules²⁰, that the axial (apical) bond is longer than the equatorial bond. In these molecules the stereochemistry about each phosphorus atom resembles a distorted trigonal-bipyramid with one nitrogen in an axial and another in an equatorial position. By analogy with the Cl^{35} NQR spectrum of molecular phosphoruspentachloride⁴, these molecules should exhibit a Cl^{35} NQR spectrum of two interactions at 29.5 and 33.7 MHz with a respective intensity ratio one to two. Unfortunately no samples of these compounds were available to test this prediction.

The compound 2,2,2-trichloro -1,3,2-dioxaphospholene, (Table 2), at 77°K exhibits a Cl^{35} NQR spectrum of three interactions of equal intensity. On the assumption of trigonal-bipyramidal stereochemistry about the phosphorus atom and by analogy with the Cl^{35} NQR spectrum of molecular phosphoruspentachloride the two interactions observed at higher frequency can be assigned to two chlorine atoms presumed equatorial, and the single low frequency interaction to a chlorine axial. Apparently then the cyclic substituent requires a comparatively tight O-P-O angle approaching 90°, in preference to approximately 120°, if it adopted a diequatorial orientation to the phosphorus atom. Most certainly there will be some distortion away from the ideal trigonal-bipyramidal model. The Cl^{35} NQR frequencies of this compound are each about two megahertz lower than their

TABLE 2

SOME CYCLIC PHOSPHORUS ESTERS AND THEIR Cl^{35} NQR FREQUENCIES AT 77°K:^a

	19.858 MHz ^b
	20.892 MHz
	27.456 MHz
	27.841 MHz ^c 31.233 MHz 31.761 MHz
2,2,2-trichloro -1,3,2-benzodioxophospholene ^d	

^a in every case the Cl^{37} NQR interaction was also observed at the appropriate frequency

^b frequency of the major peak that is sharp but shows fine structure

^c the three interactions are each of equal intensity

^d on warming the appearance of the sample changes from whitish to lemon-yellow and translucent, when the interactions become undetectable.

respective counterparts in molecular phosphoruspentachloride. This is a clear indication of the lower charge requirement of oxygen in the oxa linkage over that of the P-Cl bond. Apparently the phosphorus atom is effecting transfer of this charge difference to the chlorine atoms.

X-ray structural analyses have been reported³² for two allotropes of a 1:1 adduct of tri-isopropyl phosphite and phenanthrenequinone that is a cyclic unsaturated pentaoxyphosphorane, 2,2,2-tri-isopropoxy -4,5-(2'2"-biphenylene)- 1,3,2-dioxaphospholone. The phosphorus atom is at the centre of a PO_5 trigonal bipyramid, two isopropoxy groups are equatorial and one axial. The phenanthrenequinone moiety completes a C_2O_2P five-membered cyclic bridge between one apical and are equatorial position. Departure from ideal OP_5O angles of 90° and 120° is slight. It is likely that the 2,2,2-trichloro-1,3,2-dioxaphospholone molecule adopts the same conformation so this interpretation of the chlorine NQR spectrum is reasonable.

The Cl^{35} NQR frequencies of the two phosphorochloridites, (Table 2), are about six megahertz lower than those observed¹² for PCl_3 and $RPCl_2$. This very considerable 24% reduction demonstrates the low charge requirement of the di(R-oxa) substituent compared to either R or Cl in phosphorus (III) compounds. The one megahertz difference between these two compounds indicates a slightly greater electron releasing ability of the ethylene unit compared to that of the o-phenylene unit.

The Cl^{35} NQR frequency of o-phenylene phosphorochloridate in two megahertz lower than that of phosphoryl chloride, Table 3. This is less than the average two and one-half megahertz reduction observed on alkoxy

substitution of the latter compound: see Table 4. Thus the cyclic nature of the substitution on the phosphorus atom leads to a slight difference in the electron density at the chlorines. This observation may be the result of the cyclic substituent constraining the bond angles about the phosphorus atom, structural studies might substantiate this interpretation. X-ray diffraction studies of similar but six membered cyclic systems, the 1,3,2-dioxaphosphorinanes indicate that the P=O bond goes equatorial to the ring²¹, thus the halogen atom is axial²². In these molecules the cyclic substituent appears responsible for a considerable (circa 10°) departure from the tetrahedral bond angle about the phosphorus atom²³.

V.3. Discussion of the Chlorine-35 NQR Frequencies of Phosphoryl and Thiophosphoryl Chloride and some of their Derivatives:

The Cl³⁵ NQR frequencies of phosphoryl chloride exceeds that thiophosphoryl chloride at 77°K. In the atomic electronegativity scale oxygen is one unit higher than sulphur²⁴. Assuming that their respective inductive effects are equally transmitted by the phosphorus atom, phosphoryl chloride would be expected to have a higher chlorine NQR frequency than thiophosphoryl chloride. This reasoning presumes that the chlorine NQR frequency results from the electronic distribution of the isolated molecule alone and that there is no difference in orbital hybridization between phosphoryl and thiophosphoryl chloride.

Table 3. Cl^{35} NQR Frequencies of Phosphoryl and Thiophosphoryl Chloride^a
and their mono-phenyl Derivatives, at 77°K.

POCl_3	phosphoryl chloride ^b	28.938 MHz 28.986 MHz
PSCl_3	thiophosphoryl chloride	29.822 MHz
PhP(O)Cl_2	phenylphosphonoicdichloride ^c	26.659 MHz 26.753 MHz
PhP(S)Cl_2	phenylphosphonothioicdichloride	27.741 MHz

^a the corresponding Cl^{37} interactions were measured and found to be at precisely the predicted frequency,

^b both of equal intensity, the latter only differing by 2kHz from the reported value²⁵

^c broad and of fractionally different intensity.

There is little reported concerning the solid-state molecular structure of these low melting-point compounds. It has been suggested that phosphoryl chloride might undergo auto-coordination through intermolecular association between the phosphorus and oxygen atoms²⁶. Such a suggestion is hardly sustained by its low melting-point. This association would increase the polarity of the P=O linkage and thereby lead to a reduction in the chlorine NQR frequency.

To compare these results with the chlorine quadrupole coupling constants of microwave studies a knowledge of the asymmetry parameter is necessary. Nevertheless the solid-state quadrupole coupling constant can be estimated simply by doubling the observed chlorine NQR frequency. The resulting error being only one per-cent if the asymmetry parameter has a value of twenty-five per-cent, that is unlikely. A recent determination of

the Cl^{35} quadrupole coupling constant of a microwave study of phosphoryl chloride yielded a value of $-(55.4 \pm 1.2) \text{ MHz}^{27}$. This is 2.5 MHz lower than the value given by doubling the frequency of Table 3, and is thus remarkable in that typically the gas-state value is found to exceed the solid-state value by some five per-cent, the difference is usually attributed to intermolecular bonding²⁸. Unfortunately the microwave spectrum of thiophosphoryl chloride is insufficiently well resolved to enable an accurate determination of the quadrupole coupling constants.

Description of¹² and calculations on²⁷ phosphoryl chloride have indicated that the 3d-2p orbital interaction between phosphorus and oxygen is sufficiently large to influence its chemistry. Interchange of sulphur for oxygen is obviously going to result in electronic changes unaccounted for by their respective positions in the atomic electronegativity scale. To predict these changes is a major theoretical chemical task, however, assuming that sulphur vacant d-orbitals suitably orientated towards the phosphorus atom become sufficiently contracted²⁷ the sulphur-phosphorus $\text{dp}\pi$ bond interaction will be greater than that between phosphorus and oxygen in phosphoryl chloride. It has been suggested¹² that the vacant phosphorus 3d-orbitals can remove the negative charge on oxygen in phosphoryl chloride and also overlap with the unshared doubly occupied orbitals on the chlorine atoms. The former process was understood to predominate. From this basis alone, to account for the higher chlorine NQR frequency of thiophosphoryl chloride with respect to phosphoryl chloride, either there must be less chlorine lone-pair charge accommodated in the phosphorus orbitals or little removal of charge from the sulphur atom, in thiophosphoryl chloride. The alternatives are untenable, for the former implies a very considerable asymmetry parameter at the chlorine

atom in phosphoryl chloride, the latter, more $dp\pi$ interaction between phosphorus and oxygen orbitals of different principal quantum number than between phosphorus and sulphur orbitals of the same quantum number.

In the absence of a more thorough understanding of the electronic structure of these two molecules and of their solid-state structure, it is unreasonable to attempt to draw inference from their halogen NQR spectra of the relative electronegativities of the oxygen and sulphur atoms in this bonding situation.

The Cl^{35} NQR results of the mono-phenyl derivatives of these two compounds are also listed in Table 3. Each derivative exhibits an almost identical frequency reduction from the value of its parent compound at the same temperature. This suggests that in each compound the phenyl substituent conjugates with the halogen atom through the phosphorus atom by about the same amount.

The Cl^{35} NQR frequencies of four pairs of chlorophosphates with their corresponding chlorothiophosphates at the same temperature, are listed in Table 4. These were studied to provide further experimental information on the role of sulphur with respect to oxygen when bonded to phosphorus. Any comparison between the molecules of a pair must presume a constant geometry and that frequency variation is the result of the electronic difference of sulphur and oxygen. The general features of these five pairs along with the two pairs formed from phosphoryl and thiophosphoryl chlorides and their mono-phenyl derivatives are plotted in Figure 1.

Table 4. Cl^{35} NQR Frequencies of some Chlorophosphates and
Chlorothiophosphates, at 77°K.

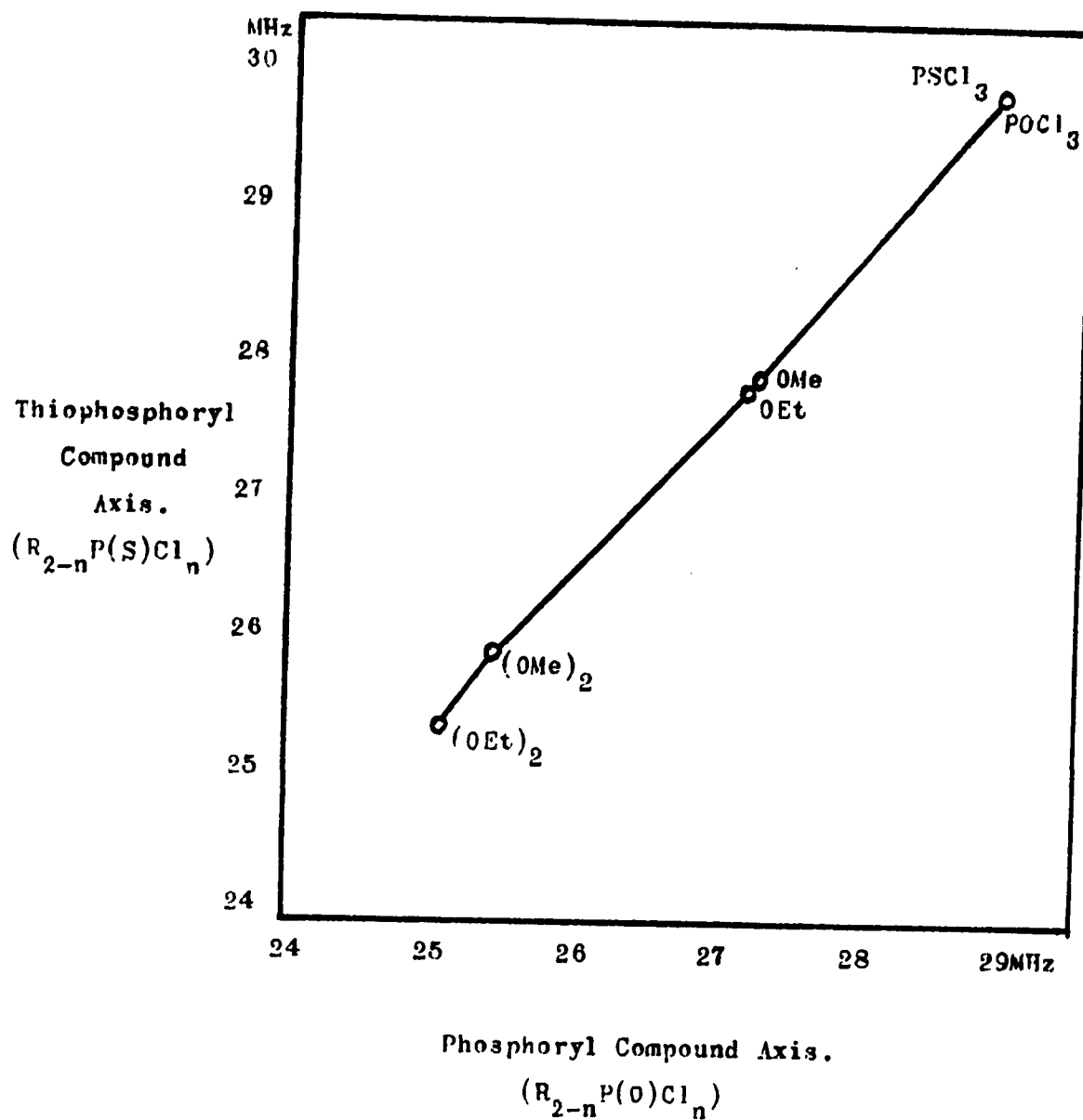
MeOP(0)Cl_2	methyl phosphorochloridate ^{a,12}	27.099 MHz 27.468 MHz
MeOP(S)Cl_2	methyl phosphorochloridothionate ^a	27.626 MHz 27.834 MHz
$(\text{MeO})_2\text{P(0)Cl}$	dimethyl phosphorochloridate	25.427 MHz
$(\text{MeO})_2\text{P(S)Cl}$	dimethyl phosphorochloridothionate	25.943 MHz
EtOP(0)Cl_2	ethyl phosphorochloridate	27.089 MHz 27.297 MHz
EtOP(S)Cl_2	ethyl phosphorochloridothionate	27.748 MHz
$(\text{EtO})_2\text{P(0)Cl}$	diethyl phosphorochloridate ^b	25.08 MHz
$(\text{EtO})_2\text{P(S)Cl}$	diethyl phosphorochloridothionate	25.409 MHz
$(\text{iPrO})_2\text{P(S)Cl}$	diisopropyl phosphorochloridothionate	25.732 MHz

^a two interactions of equal intensity.

^b broad interaction, weak due to limited crystallinity.

Figure 1.

Plot of the Cl^{35} NQR Frequencies for Five Complementary Pairs of Molecules: Phosphoryl and Thiophosphoryl Chloride, Four Chlorophosphates and Four Chlorothiophosphates.



Alkoxy substitution reduces the Cl^{35} NQR frequency following in inverse order the length increase of the alkyl chain. Dialkoxy substitution is even more effective. The approximate linearity of the plot indicates the similarity of the effect of alkoxy substitution in either the chlorophosphate or chlorothiophosphate series. The slope of the plot away from the sulphur containing compound axis, particularly in the low frequency region, suggests the chlorophosphate system is slightly less capable of transmitting an overall inductive effect between the substituent and the remaining chlorine atoms, than is the chlorothiophosphate system. This observation becomes more obvious when the frequency reduction on alkoxy substitution is considered as a per-centage of the initial value of the parent compound of the respective series.

Chlorine NQR studies of phosphoryl and thiophosphoryl chlorides, their mono-phenyl derivatives and eight esters that together form four complementary pairs all demonstrate the greater overall electronegativity of the sulphur compared to the oxygen atom in the same bonding situation, contrary to their respective positions in the atomic electronegativity scale. This is probably the result of sulphur atom d-orbital involvement. It is further observed from the two series that the derivatives can conjugate with themselves through the phosphorus atom. Possibly this conjugation is slightly greater for the thiophosphate system. There is no evidence for direct conjugation with the $\text{P}=\text{O}$ or $\text{P}=\text{S}$ bond.

V.4. The Chlorine NQR Spectra of Some Compounds Containing the Trichloro-phosphazo group:

The purpose of the study of these compounds was to gain some insight

of the difference in electronic structure of the linear and cyclic $(\text{NPCl}_2)_n$ systems from chlorine NQR. The parent molecules of some N-P polymeric systems terminating with the trichlorophosphazo group, $(\text{Cl}_3\text{PN}=\cdot)$, were prepared and examined. Due to the extreme reactivity of these linear compounds and the complexity of their chlorine NQR spectra this aim could not be achieved.

Trichlorophosphazosulphonyl chloride, $\text{Cl}_3\text{PNSO}_2\text{Cl}$, and trichlorophosphazophosphoryl chloride, $\text{Cl}_3\text{PNPOCl}_2$, have already been the subject of a chlorine NQR study at the temperature of liquid nitrogen, in this laboratory, and the results reported¹. The Cl^{35} NQR spectrum of $\text{Cl}_3\text{PNPOCl}_2$ consists of five interactions at an average frequency of 26.8 MHz and a further ten interactions at an average frequency of 30.1 MHz. The latter set was assigned to the chlorines of the trichlorophosphazo group of the molecule. The reported interpretation of the Cl^{35} NQR spectrum of $\text{Cl}_3\text{PNSO}_2\text{Cl}$ was found to be in error following a temperature dependence and line-width investigation, (c.f., Chapter III herein). Three Cl^{35} interactions at an average frequency of 30.7 MHz are assigned to the chlorines of the trichlorophosphazo group of the molecule.

The compound μ -nitrobistrichlorophosphonium hexachlorophosphate, $[\text{Cl}_3\text{PNPCl}_3]^+ [\text{PCl}_6]^-$, was prepared³⁰ and examined in anticipation of it providing information of the Cl^{35} NQR frequency increase for the cation over that of the uncharged trichlorophosphazo group. At 77°K the Cl^{35} NQR spectrum consists of approximately forty-one separate interactions of relatively similar and low intensity, spread throughout the frequency range 29.2 to 31.4MHz.

Considering that the hexachlorophosphate ion exhibits a Cl^{35} NQR spectrum in the frequency range 28.4 to 30.5 MHz, obviously the observed spectrum results from both ions. At room temperature the spectrum is still complex unresolved and much weaker. To facilitate recognition of the spectrum of the cation alone various possibilities of replacement of the counter-ion were considered and substitution by the hexachloroantimonate ion attempted. The reported procedure³¹ gave the intended product in low yield and work was discontinued.

The next compound of this P-N linear polymeric series, $[\text{Cl}_3\text{PNPCl}_2\text{NPCl}_3]^+ [\text{PCl}_6]^-$, was prepared following the reported procedure³¹.

The importance of the compound to this study is its potential ability to provide information of the frequency of the internal chlorine atoms for comparison with the chlorines of the cyclic system, $(\text{NPCl}_2)_n$. Although this compound was prepared and studied when in excellent condition, as indicated by its infrared spectrum, no quadrupolar interactions could be detected. It appeared to rapidly decompose even when sealed under vacuum and stored in liquid nitrogen, to give hydrogenchloride gas and possibly cyclize.

These studies have indicated that the average Cl^{35} NQR frequency for the trichlorophosphazo group, of these compounds at 77°K, is $(30.4 \pm 3)\text{MHz}$, one half a megahertz above that of the thiophosphoryl chloride molecule of similar geometry at the phosphorus atom. The charge of this group can become delocalized over the system to which it is connected, thus possibly accounting for its observed higher Cl^{35} NQR frequency. In the case of the μ -nitrobistrichlorophosphonium cation, the trichlorophosphazo group has an additional share

of half a positive charge. Each of the three chlorines must experience some of this, for the Cl^{35} NQR frequency of the entire molecule at 77°K does extend above that reported for the hexachlorophosphate anion and the average value mentioned above, by one megahertz. These frequencies are two megahertz in excess of those observed for the cyclic $(\text{NPCl}_2)_n$ polymers discussed in Chapter 2. This observation concurs with the concept of their chlorines bonded to phosphorus, that is considered as being part of a system of delocalized charge.

CHAPTER V

References

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CHAPTER VI.

CHLORINE NQR STUDIES OF SOME SULPHUR-CHLORINE COMPOUNDS

VI.1. Discussion of Cl^{35} NQR Frequencies of the S-Cl Bond for the Various Sulphur Atom Formal Valence States.

The sulphur atom exists in several formal valence states and in a variety of bonding situations. Interpreting its chemical bonding has attracted much attention and controversy¹. Due to its high electron affinity, in lower valence states other than its elemental form, it is unstable to oxidation. The coordination about the sulphur atom in its compounds is tetrahedral except in the sulphur hexahalides, sulphur tetrafluoride² and thionyl tetrafluoride, a distorted trigonal-bipyramid³. Sulphur chemical bonding has the added complexity of d-orbital involvement that cannot be ignored except in divalent sulphur and the simple halides.

Few spectroscopic techniques yield bonding information about sulphur. Its most common magnetic isotope, S^{33} , is of very low abundance. The technique of X-ray induced electron emission spectroscopy has been applied to sulphur inner and outer shell electrons to yield ionization energies, chemical shifts⁴ and estimation of the number of valence electrons⁵, respectively. The electron spin resonance spectra of some sulphone radical anions have been observed and interpreted⁶ as has the ultraviolet absorption spectrum of dibenzothiophene and some of its isologues, in terms of LCAO-MO theories⁷.

This chapter describes the use of the chlorine nuclear quadrupole of the sulphur-chlorine bond as a charge probe of the sulphur atom bonding. This is a first step for only the hexavalent sulphur-chlorine bonding situation is considered fully. Similar information is required for quadrivalent and divalent sulphur before qualitative comparisons can be made. As molecular orbital calculations on sulphur bonding are as yet incomplete only a qualitative description is presented.

The Cl^{35} NQR frequencies observed for the S-Cl bond range from 29.5 to 42.9 MHz for ethane sulphonyl chloride and SCl_3^+ respectively. This is only slightly less than the extrema of the C-Cl³⁵ bond range of 28.3 to 43.6 MHz, observed for pivaloyl chloride and dichlorodicyanomethane and discussed elsewhere in this Thesis. Unlike carbon, sulphur exists in several valence states and would be expected to exhibit a greater S-Cl³⁵ NQR frequency range. Apparently the sulphur atom fails to transmit the electronic effects of its substituent in the manner of carbon.

The relative overall electronegativity of the sulphur bond orbital to chlorine in the full range of sulphur-chlorides can be inferred from the Cl^{35} NQR frequencies listed in Table 1. The various Cl^{35} NQR frequencies of Table 1 are reasonable. The frequency variations of these compounds are the result of three principal effects: 1) the varying s-character of the sulphur orbital to chlorine, 2) the bonding between the substituent, other than chlorine, which replaces the lone-pair and 3) the total inductive effect of the substituents. Consider the sulphur-chlorine series: SCl_2 differs from SCl_4 and SF_5Cl in that its sulphur bond orbitals will be low in d-orbital

Table 1: Cl^{35} NQR Frequencies of the Chlorides of Sulphur.

$\ddot{\text{S}}\text{Cl}_2$	37 MHz ^a	$\ddot{\text{S}}\text{Cl}_2$	37 MHz ^a	$\text{R}\ddot{\text{S}}\text{Cl}$	37 MHz
$\ddot{\text{S}}\text{Cl}_4$	42 MHz ^b	$\ddot{\text{S}}\text{OCl}_2$	32.5 MHz	$\text{R}\ddot{\text{S}}\text{OCl}$	29.5 MHz
SF_5Cl	40 MHz ^c	SO_2Cl_2	37.7 MHz	RSO_2Cl	32.5 MHz

The dots on the sulphur atoms indicate electrons in lone-pair orbitals.

^a estimated from the observed value of S_2Cl_2 . ^b estimated from the observed value of SCl_3^+ . ^c estimated from the microwave study¹³.

contribution. SCl_4 has a higher frequency due to increased chloro-substitution but is a compromise due to reduction from fall in orbital s-character over that of SCl_2 . SF_5Cl is even lower despite increased substitution, due to the presumed lower electronegativity of its sp^3d^2 hybrid orbitals. The members of the oxychloride series are at lower frequency as a result of the lower electronegativity of the sulphur hybrid orbital to chlorine, due to the hybridization requirements of the double bond. The almost thirteen megahertz drop from SCl_4 to RSOCl is the result of the necessary inclusion of d-orbital hybridization to provide the π -type overlap to oxygen. The different sulphur atom orbital hybridization of SO_2Cl_2 and the additional oxygen atom inductive effect results in a five megahertz increase. The R (organo) substituted series frequencies are not greatly different from those of the oxychloride series as these differ only in replacement of a chlorine of the latter with R of the former.

VI.2. Discussion of the NQR Frequencies of Sulphenyl and Sulphinyl Chlorides.

Table 2. Chlorine NQR Frequencies of Some Sulphenyl and Sulphinyl

Chlorides at 77°K.

		Cl ³⁵ NQR MHz	Cl ³⁷ NQR MHz
C ₆ H ₅ SCl	benzenesulphenyl chloride	37.011	29.170
4-FC ₆ H ₄ SCl	4-fluorobenzenesulphenyl chloride	37.802	29.796
4-ClC ₆ H ₄ SCl	4-chlorobenzenesulphenyl chloride	40.433 (34.975) ^a	31.864 (27.566) ^a
4-CH ₃ C ₆ H ₄ SCl	4-toluenesulphenyl chloride	38.493	30.335
2,4-(NO ₂) ₂ C ₆ H ₃ SCl	2,4-dinitrobenzenesulphenyl chloride	37.012	29.175
CF ₃ SCl	trifluoromethanesulphenyl chloride	42.196	33.255
CCl ₃ SCl	trichloromethanesulphenyl chloride	39.412 39.527 39.610 ^b 39.825 39.868 39.921 40.043	31.063 31.154 31.212 31.387 31.421 31.464 31.560
S ₂ Cl ₂	sulphur monochloride	35.584 ^c 35.977	28.047 28.358
C ₂ H ₅ SOCl	ethane sulphinyl chloride	29.477	23.233
SOCl ₂	thionyl chloride	31.884 ^d 32.088	25.130 25.291
SCl ₃ ⁺	cation of Cl ₉ SSb compound	42.185 42.932	33.839 33.249

^a chlorine bonded to carbon ^b twice the intensity of the other Cl³⁵ interactions of this compound, all other interactions for either isotope of any compound are of equal intensity ^c both Cl³⁵ interactions are about 20 kHz below those reported^d 3kHz below the reported values⁸.

In addition to the arylsulphenyl chlorides listed in Table 2

a number of alkylsulphenyl chlorides were also examined. Despite careful crystallization the highly coloured reactive liquids failed to yield interactions. The trihalomethanesulphenyl chlorides were exceptions. The Cl^{35} NQR spectrum of trichloromethanesulphenyl chloride has been reported⁹, but apparently it was not resolved as three interactions of non-integral intensities were observed. The Cl^{35} NQR at 39.610 MHz is twice the intensity of the other six. This can be interpreted as indicating that there are $2n$ molecules per unit cell at 77°K and the chlorine atoms are distributed equally amongst eight sites. Apparently the electric field gradient at two of these sites coincides at that temperature. No other Cl^{35} interactions could be located over a wide frequency range so presumably one of these interactions is due to the chlorine bonded to sulphur. This chlorine will have a different temperature coefficient of NQR frequency from the methyl chlorines due to the different moments of inertia of its vibrational modes and should be identifiable by a temperature dependence study. This was not undertaken due to the low melting point of the compound limiting the observable range of the NQR spectrum. The Cl^{35} NQR frequency of trifluoromethanesulphenyl chloride is two megahertz above the presumed region of that of trichloromethane sulphenyl chloride reflecting the greater inductive effect of the trifluoromethane group*. Solid sulphur monochloride is presumed to have the hydrogen peroxide type structure nevertheless there is some support for the thiothionyl molecular configuration¹⁰. Its Cl^{35} NQR frequency, almost five megahertz above that of thionyl chloride, overrules the latter molecular formulation. Samples of sulphur dichloride, freshly distilled over phosphorus trichloride, failed to yield interactions over a wide frequency range. Nothing is reported of its molecular structure in the solid-state.

* In the +I series, F is greater than Cl; then $\text{F}_3\text{C}-$ is greater than $\text{Cl}_3\text{C}-$, see M.J.S.Dewar, 'Electronic Theory For Organic Chemistry', Clarendon Press, Oxford, 1954, p.52.

The chlorine NQR frequencies of the arylsulphenyl chlorides of Table 2 show no trend typical of the nature or position of the substituent, unlike their sulphonyl counterparts, vide infra. Nitro groups situated ortho and para are known for their electronic effects on the benzenoid system yet ortho,para-dinitrobenzenesulphenyl chloride has an almost identical chlorine NQR frequency to benzenesulphenyl chloride. An ortho nitro group oxygen might be interacting with the sulphur to form a five membered cyclic system, this would reduce the charge requirements of the sulphur and thus account for the observed low frequency. Examination of purified, recrystallized, sublimated and fused samples of ortho-nitrobenzenesulphenyl chloride over a wide frequency range at different temperatures revealed no interactions. The two and one-half megahertz chlorine NQR frequency increase of para-chlorobenzenesulphenyl chloride over the para-fluoro analogue is unusual. Qualitative interpretation of these results would be facilitated by knowledge of the molecular structures.

The only alkylsulphinyl chloride studied, C_2H_5SOCl , yielded a Cl^{35} NQR two and one-half megahertz below that of $SOCl_2$. Both compounds have already been discussed. An apparently good sample of benzenesulphinyl chloride, that crystallized readily, failed to give any interaction. The results for the inferred ion, SCl_3^+ , are included in Table 2. Recently some better evidence, from vibrational spectroscopic studies, for its existence was reported¹¹ for the same compound studied here¹². The chlorine NQR spectrum of Cl_9SSb that is discussed elsewhere in this Thesis favours such an ionic formulation to the exclusion of any other possibilities. As was previously mentioned, the three highly inductive substituents, the positive charge and the simple sp^3 hybrid bonding, unlike that of the thionyl and substituted thionyl chlorides, together result in its high chlorine NQR frequencies.

The existence of sulphur tetrachloride in the solid-state has been suggested, however more recent studies¹² have not been confirmatory. By analogy with the other Group VI tetrahalides it would be ionized to $\text{SCl}_3^+\text{Cl}^-$. The SCl_3^+ ion has here been presumed tetrahedral, however, the sulphur tetrachloride molecule might not be, for the sulphur tetrafluoride molecule in the liquid is understood to be non ionized and as a trigonal bipyramid¹³. Organic sulphur trichlorides, RSCl_3 , have been reported, but all decomposed on warming to room temperature¹⁹. Analogously these would be expected to yield Cl^{35} NQR at about forty megahertz.

A small quantity of sulphur chloride pentafluoride gas was frozen and examined unsuccessfully over a considerable frequency range. The microwave study of this gas¹⁴ including a determination of the Cl^{35} quadrupole coupling constant that was found to be about -81.5 MHz. From this determination the Cl^{35} NQR frequency for the solid at 77°K is estimated to be about 40 MHz. This is two megahertz greater than that of sulphuryl chloride, SO_2Cl_2 , of the same sulphur formal valence state but of very different orbital hybridization.

VI.3. Discussion of the Cl^{35} NQR Frequencies of Some Sulphonyl Chlorides.

In a series of compounds that can be considered as derivatives of sulphuryl chloride with substitution of one of its chlorines, the remaining chlorine exhibits NQR frequency variation with different substituents. The Cl^{35} NQR results for almost fifty molecules differing in R, in the system RSO_2Cl , will now be presented. Through consideration of the frequencies of various related molecules of the series a qualitative description of some of the electronic properties of the sulphur atom in the sulphone group is developed. Unless otherwise

indicated the samples employed in this study were of commercial origin. Care was taken to ensure correct isotope assignment of the observed chlorine quadrupolar interactions listed in the following tables.

VI. 3.i. The Compounds RSO_2Cl where R is Other than an Aryl Group.

Table 3: Cl^{35} NQR Frequencies in MHz of Some Alkyl and Substituted Alkyl Sulphonyl Chlorides at 77°K .

		S-Cl	C-Cl
methanesulphonyl chloride	$\text{CH}_3\text{SO}_2\text{Cl}$	33.228	
ethanesulphonyl chloride	$\text{CH}_3\text{CH}_2\text{SO}_2\text{Cl}$	32.519 ^a	
n-propanesulphonyl chloride	$\text{n-CH}_3\text{CH}_2\text{CH}_2\text{SO}_2\text{Cl}$	32.134	
n-butan sulphonyl chloride	$\text{n-CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{Cl}$	32.759 ^a	
3-chloropropanesulphonyl chloride	$\text{Cl-CH}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{Cl}$	32.359	33.981
benzylsulphonyl chloride	$\text{C}_6\text{H}_5\text{CH}_2\text{SO}_2\text{Cl}$	32.982	
1,2-ethylenebis(sulphonylchloride)	$\text{ClSO}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{Cl}$	34.232	
chlorosulphonylacetylchloride	$\text{ClOCCH}_2\text{SO}_2\text{Cl}$	34.951 35.191	31.973 32.510
trichloromethanesulphonyl chloride	$\text{Cl}_3\text{CSO}_2\text{Cl}$	36.276	40.742 40.971 41.192

^a observed at exactly the same frequency as reported in reference 13
all Cl^{35} interactions of any one compound were of equal intensity.

Table 3 lists the Cl^{35} NQR frequencies determined for some alkyl sulphonyl chlorides at 77°K . In the series that R is ethane, n-propane, n-butane, 3-chloropropane and benzyl, the frequency is approximately constant

and less than that of methanesulphonyl chloride. This suggests that for a greater alkyl chain than R being ethane, its sigma bond inductive effect transmitted by the sulphur atom to the sulphone group and experienced by the chlorine is constant. In 1,2-ethylenebis(sulphonyl chloride) the enhanced frequency indicates that the sigma bond inductive effect of the chlorosulphonyl groups are transmitted through the carbon chain. In chlorosulphonylacetyl chloride in which the inductive groups are separated by only one carbon atom the frequency is still higher. The competition for sigma bond charge between the chlorosulphonyl group and the substituent is even more extreme in trichlormethane sulphonyl chloride in which the Cl^{35} NQR frequency of the latter group is within one megahertz of that of sulphuryl chloride.

Examination of single crystals of this compound grown by vacuum sublimation and using Cu K α radiation and a Weissenberg Camera revealed only thirty-six independent reflections on zero-level exposure along the needle axis at room temperature, some one-hundred and fifteen degrees below its reported melting point. This is strong evidence for the presence of considerable molecular motion at room temperature. At -76°C the intense quadrupolar interactions observed at -196°C are undetectable. Also at the former temperature the low-temperature whiteish appearance of the compound is replaced by translucency. Onset of large-scale molecular motion by the groups, between the above two temperatures, is considered responsible for the non-observation of the chlorine NQR spectrum in the 30 to 40 MHz region at higher temperatures.

Table 4: Cl^{35} NQR Frequencies in MHz of Some Halo and Oxysulphonyl Chlorides at 77°K.

fluorosulphuryl chloride	FSO_2Cl	39.350
sulphuryl chloride	ClSO_2Cl	37.597 ^{a,b} 37.810
chlorosulphonic acid	HOSO_2Cl	37.555
ethoxysulphonyl chloride	$\text{C}_2\text{H}_5\text{OSO}_2\text{Cl}$	35.659
pyrosulphuryl chloride	$\text{ClSO}_2\text{OSO}_2\text{Cl}$	38.847 ^a 39.294

^a both interactions are of equal intensity ^b reported at 14 kHz higher frequency with an indeterminacy of $\pm$ the quench rate (unstated)¹⁶.

Table 4 lists the Cl^{35} NQR frequencies of some halo and oxysulphonyl chlorides. The greater electronegativity of fluorine compared to chlorine is reflected in an almost two megahertz increase in the Cl^{35} NQR frequency of sulphuryl chloride on monofluoro substitution. The proximity of the former compound's frequency to that of chlorosulphonic acid indicates the similar electronegativity of the hydroxyl group to chlorine in the sulphone system. The Cl^{35} NQR frequencies of the salts of this acid will give an indication of the amount of charge of the hydroxyl oxygen held by the proton, through the decrease in frequency. Probably this is little and by analogy with chloranilic acid and its salts, discussed elsewhere in this Thesis, the Cl^{35} NQR is predicted at about thirty-four megahertz. An X-ray structural determination of NOSO_2Cl has revealed the SO_3Cl^- ion to be a slightly flattened pyramid of C_{3v} symmetry¹⁷.

The substituted oxygen on the sulphone group must be capable of transmitting the inductive effect of its moiety, for the alkyl chain of ethoxysulphonyl chloride appears responsible for its two megahertz frequency drop from that of chlorosulphonic acid. In pyrosulphuryl chloride, (disulphuryl chloride), there must be considerable competition for sigma bond charge as its frequency approaches that of fluorosulphuryl chloride and is about five megahertz above that of 1,2-ethylenebis(sulphonyl chloride).

Table 5: Cl^{35} NQR Frequencies in MHz of Four N-Substituted N-Sulphonyl Chlorides at 77°K .

amidosulphonyl chloride	$\text{H}_2\text{NSO}_2\text{Cl}$	34.465 ^{a,b} 35.110
dimethylsulphamoyl chloride	$(\text{CH}_3)_2\text{NSO}_2\text{Cl}$	32.294
chlorosulphonyl isocyanate	OCNSO_2Cl	37.655 ^a 37.807
trichlorophosphazosulphonyl chloride	$\text{Cl}_3\text{PNSO}_2\text{Cl}$	32.715 ^c

^a both interactions of equal intensity ^b prepared following reference 18, observed on a DECCA instrument due to lattice-elastic interactions with frequency modulation ^c S- Cl^{35} interaction, the chlorine NQR spectrum and preparation of this compound is discussed in Chapter III of this Thesis.

Table 5 lists the Cl^{35} NQR frequencies of four N-substituted N-sulphonyl chloride molecules of two types of orbital hybridization at the nitrogen atom. In dimethylsulphamoyl chloride and amidosulphonyl chloride

the nitrogen lone-pair can be considered in either a π or a tetrahedral hybrid orbital. The latter is energetically favoured but limits the transfer of electron density between N and S to sigma bonding. The Cl^{35} NQR frequency of dimethylsulphamoyl chloride is very low for the RSO_2Cl series, indicating charge release into the sulphone group through the sigma bond framework by the methyl groups. Further there will be S-Cl π -bonding contributing to the observed low frequency in the absence of competition from N-S π -bonding. This rationalization suggests that the Cl^{35} NQR of the diethyl analogue will be found at even lower frequency. The frequency of amidosulphonyl chloride is much higher, for the nitrogen atom is devoid of charge releasing groups to satisfy the sulphone system.

The orbital hybridization of nitrogen in the remaining two molecules of Table 5 is quite different. It is probable that the N-S bond axis of chlorosulphonyl isocyanate will make an angle of slightly more than 120° with the axis of the linear isocyanate chain. Such geometry has been recognized in methylisocyanate²⁰, cyanic acid²¹, germylisocyanate²², chlorine isocyanate²³ but silylisocyanate might be an exception²⁴. The hybridization at the nitrogen atom will be trigonal including the lone-pair and a single electron in a π -orbital. Calculations of this nitrogen hybridization state, described in Chapter VII of this Thesis, indicate that the nitrogen π orbital in the isocyanate group is an effective charge acceptor. These factors together suggest that the high Cl^{35} NQR frequency of chlorosulphonyl isocyanate is anomalous. However, the calculations on chlorine isocyanate indicate that the nitrogen sigma bond orbital exerts a considerable inductive effect. It is likely that this is also experienced by the chlorosulphonyl group of chlorosulphonyl isocyanate. This would account for its apparently high Cl^{35} NQR frequency.

The remaining molecule of Table 5, trichlorophosphazosulphonyl chloride, was the subject of a detailed study described in Chapter III of this Thesis. The hybridization on the nitrogen might also be presumed trigonal, including the lone-pair and with an electron in a π -orbital. The S-Cl³⁵ NQR frequency of this molecule is five and one-half megahertz less than that of chlorosulphonyl isocyanate, reflecting the inability of the P-N system to transmit the large inductive effect of the phosphazo chlorines to the sulphone system.

VI. 3. ii, The Compounds RSO₂Cl where the Substituent R is an Aryl Group.

Listed in Table 6 are the Cl³⁵ NQR frequencies of some methylbenzenesulphonyl chlorides along with that of benzenesulphonyl chloride of 32.537 MHz . This is one of three values quoted in a study of this molecule, that were ascribed to different crystalline phases¹⁵. This single interaction only, was observed after various treatments of the compound. It is likely that the reported spectrum is the result of misinterpretation of sidebands from the use of a super-regenerative oscillator. The same report lists four interactions of various intensities for the 2,5-dimethylbenzenesulphonyl chloride compound, probably as a result of similar difficulty.

Table 6. Cl^{35} NQR Frequencies in MHz of Some Methylbenzenesulphonyl Chlorides and p-Methoxybenzenesulphonyl Chloride at 77°K.

$\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$	32.537	various values reported, see text
4- $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{Cl}$	32.457	3 kHz less than reported, ref.25
2,5-(CH_3) ₂ - $\text{C}_6\text{H}_3\text{SO}_2\text{Cl}$	32.268	various values reported, see text
2,4-(CH_3) ₂ - $\text{C}_6\text{H}_3\text{SO}_2\text{Cl}$	32.064 32.330	both of equal intensity average, 32.197
2,4,6-(CH_3) ₃ - $\text{C}_6\text{H}_2\text{SO}_2\text{Cl}$	31.702	
4- $\text{CH}_3\text{O} - \text{C}_6\text{H}_4\text{SO}_2\text{Cl}$	32.592	

The Cl^{35} NQR frequencies of all the methylbenzenesulphonyl chlorides are lower than benzenesulphonyl chloride. The lowering follows increased methyl substitution. The methyl group is well known as a releaser of charge into sigma bond systems, apparently here it is transmitted from the aromatic system to the sulphone group. The methyl group appears most effective in the 2 or ortho position considering the half megahertz drop from the 2,4-dimethyl compound to the 2,4,6-trimethyl one. Unfortunately no interaction could be detected in even freshly distilled fractions of 2-methylbenzenesulphonyl chloride that never readily or completely crystallized. The frequency of the 4-methoxy compound is close to that of benzenesulphonyl chloride. Apparently the effect of the methoxy group on the charge density of the aromatic system, as indicated by the chlorine of the sulphone group para, is little different from that of a proton.

The Cl^{35} NQR frequencies of some halobenzenesulphonyl chlorides are listed in Table 7. There is evident a diminishing frequency increase on successive halo substitution at the 4 or para position. Since the inductive effect of the halogen atoms diminishes on proceeding down the halogen series, the frequency shift should parallel and not oppose this trend. However, the halogen atom conjugative effect increases on proceeding down the series, and would increasingly limit S-Cl π -type bonding. This process predominates in the overall ordering of the respective frequencies. As is to be expected, pentafluoro substitution results in a very considerable Cl^{35} NQR frequency increase.

The S-Cl Cl^{35} NQR frequencies of the dichloro compounds exceed that of the monochloro one, but those of the trichloro compounds are raised little further. Thus S-Cl frequency increase on successive chloro substitution is far from additive. A more regular increase is evident in the C-Cl NQR frequencies or their average values. Clearly the sulphonyl chlorine is not directly reflecting the change in charge density at the site of sulphone substitution in the aromatic system, from which it is one atom removed.

The C-Cl Cl^{35} NQR frequencies of the multichlorobenzenes of Table 7 are regular in that their average values directly reflect increased chloro substitution. The average of the 3,5-dichloro-2-hydroxy compound is close to those of the two trichloro compounds, for the inductive effect of the hydroxyl group is similar to that of chlorine. The apparent irregularity of the S-Cl Cl^{35} NQR frequencies presents a sharp contrast. These however can be qualitatively accounted for through consideration of their respective quinoidal classical molecular formulations. The five molecules fall into

Table 7. Cl^{35} NQR Frequencies in MHz of Some Halobenzenesulphonyl Chlorides
at 77°K .

	S-Cl	C-Cl	average (C-Cl)
4-FC ₆ H ₄ SO ₂ Cl	32.796		
4-ClC ₆ H ₄ SO ₂ Cl	32.831 ^a	35.971 ^a	
4-BrC ₆ H ₄ SO ₂ Cl	32.890 ^b		
4-IC ₆ H ₄ SO ₂ Cl	32.889		
C ₆ F ₅ SO ₂ Cl	35.150		
2,5-Cl ₂ C ₆ H ₃ SO ₂ Cl	34.446 ²	36.388 ^a 37.320	36.854
3,4-Cl ₂ C ₆ H ₃ SO ₂ Cl	33.029	36.614 36.853	36.734
3,5-Cl ₂ ,2-(OH)-C ₆ H ₂ SO ₂ Cl	34.684	36.204 37.351	36.778
2,3,4-Cl ₃ C ₆ H ₂ SO ₂ Cl	33.267	37.336 37.584 38.373	37.764
2,4,5-Cl ₃ C ₆ H ₂ SO ₂ Cl	34.309	37.071 37.615 38.123	37.603

^a all Cl^{35} interactions for any one compound are of equal intensity
and identical to the values reported in reference 26

^b five kHz below the value reported in reference 26.

two groups depending on whether or not the sulphone system can be considered as part of a benzoquinone type system. In the 3,4-dichloro and 2,3,4-trichloro compounds the quinoidal system confines the otherwise fully delocalized or π charge density to filled molecular orbitals on carbons 2 and 3,5 and 6, and thus also on carbon 1 and the sulphur atom. Although this will reduce the S-Cl π -bonding it also leads to release of charge in the carbon sigma orbital to the sulphone group, therefore the S-Cl NQR frequencies of these two molecules are low. Additional chloro substitution in the 2-position of the former has little effect on the NQR frequency of the sulphonyl chlorine. In the other three multichlorobenzenes the S-Cl NQR frequency is in contrast high. In each, carbon 1 bonded with sulphur, is the site of one end of a quinoidal type bond or pair of filled molecular orbitals with either carbon 2 or 6. Thus for the reasons that the former two multichlorobenzene molecules have low S-Cl NQR frequencies those of the latter three are relatively high. Chlorosubstitution on carbon 4 of the 2,5-dichloro compound results in a small decrease in S-Cl NQR frequency for the quinoidal type bonding is weakened. Now instead of being strictly 1 and 6,3 and 4, it must be mostly but not exclusively 1 and 2,4 and 5. The S-Cl NQR frequency of the 3,5-dichloro-2-hydroxy molecule is slightly higher than that of the 2,3,5-trichloro one for the same reason that the 2,5-dichloro molecule is lower. The 2-hydroxy group firmly confines the quinoidal type bonding to 1 and 6,3 and 4.

Table 8. Cl^{35} NQR Frequencies in MHz of Some Nitrobenzenesulphonyl Chlorides at 77°K

	S-Cl	C-Cl
$2-(\text{NO}_2)-\text{C}_6\text{H}_4\text{SO}_2\text{Cl}$	34.315	
$3-(\text{NO}_2)-\text{C}_6\text{H}_4\text{SO}_2\text{Cl}$	34.340 ^a	
$4-(\text{NO}_2)-\text{C}_6\text{H}_4\text{SO}_2\text{Cl}$	33.434 ^a	
$2,4-(\text{NO}_2)_2-\text{C}_6\text{H}_3\text{SO}_2\text{Cl}$	34.791	
$4-\text{Cl}, 2-(\text{NO}_2)-\text{C}_6\text{H}_3\text{SO}_2\text{Cl}$	34.647	36.394
$4-\text{Cl}, 3-(\text{NO}_2)-\text{C}_6\text{H}_3\text{SO}_2\text{Cl}$	34.440	36.504

^a observed at 3 kHz less than the reported value, ref. 26.

The Cl^{35} NQR frequencies of some nitrobenzene sulphonyl chlorides are listed in Table 8. In all but one of the molecules the S- Cl^{35} NQR frequency is about two megahertz greater than that of benzenesulphonyl chloride. As is to be expected, di-nitro substitution raises the Cl^{35} NQR frequency still higher. Clearly the nitro group is exerting a considerable sigma bond inductive effect that is transmitted through the sulphone group to the chlorine. The 4-position chlorosubstituted 2 and 3 nitrobenzene molecules exhibit a small Cl^{35} NQR frequency increase in comparison with their respective unsubstituted nitrobenzenesulphonyl chlorides. Also the frequencies of the carbon-chlorines are less than the respective average values of their dichlorosubstituted analogues of Table 7. Considering the highly inductive nature of the nitro group the C- Cl^{35} NQR would reasonably

be expected at one megahertz higher frequency. Apparently this group influences the charge density of the aromatic system by more than a sigma bond inductive process.

The result for 4-nitrobenzenesulphonyl chloride in Table 8 is remarkable for being at one megahertz lower frequency than that of either the 2 or 3-position isomers. Unfortunately there were no substituted 4-nitrosubstituted benzenesulphonyl chlorides, other than 2,4-dinitrobenzenesulphonyl chloride, available for study. The frequency of this molecule is not greatly above that of either the 2 or 3-mononitrosubstituted isomers, thus implying that its 4-position nitro group is having a lesser effect on the S-Cl NQR frequency than is to be expected of such an inductive group*. This observation is reasonable considering that the nitro group at this position conjugates strongly with the aromatic system that then must be in conjugation with the sulphone group. Such an explanation also predicts a similarly lowered frequency for the 2-position isomer that is however little different from that of the 3-nitro isomer. The explanation requires the nitro group to be coplanar with the aromatic system. For the 2-position isomer this conformation would result in steric interaction of adjacent bulky groups.

The Cl^{35} NQR frequencies of some benzenesulphonyl chlorides substituted with halosulphone or similar groups are listed in Table 9. The spectrum of 3-chlorosulphonylbenzenesulphonyl chloride at 77°K has a pair of interactions separated by 200 kHz at about 33.8 MHz which is reasonable.

*Positive inductive, recognizing its sigma-bond electron withdrawing ability. Overall, this group has a -E effect on the π -electron system by conjugation. See, M.J.S. Dewar, 'Molecular Orbital Theory for Organic Chemistry', Chap., 9.12, McGraw-Hill, New York, 1969.

Table 9. Cl^{35} NQR Frequencies in MHz of Some Carboxy and Sulphone
Substituted Benzenesulphonyl Chloride Molecules at 77°K.

3-(ClSO_2)- $\text{C}_6\text{H}_4\text{SO}_2\text{Cl}$	polycrystalline and fused sample:	33.708 ^a 33.902 ^a 34.448 ^a	34.019
3-chlorosulphonylbenzenesulphonyl chloride			
1,3,5-(ClSO_2) $_3\text{C}_6\text{H}_2\text{SO}_2\text{Cl}$	fused sample:	33.564 ^b 33.767 ^b 34.798 ^b	34.043
1,3,5-benzenetrisulphonyl chloride			
2-(FSO_2)- $\text{C}_6\text{H}_4\text{SO}_2\text{Cl}$	polycrystalline; fused sample:	33.782 33.963	
2-fluorosulphonylbenzenesulphonyl chloride			
3-(COOH)- $\text{C}_6\text{H}_4\text{SO}_2\text{Cl}$	polycrystalline sample:	33.757 (33.672) ^c	
3-carboxylicacidbenzenesulphonyl chloride			
4-Cl,3-(COOH) $\text{C}_6\text{H}_3\text{SO}_2\text{Cl}$		34.004	(37.321 of C-Cl^{35})
4-chloro,3-carboxylicacidbenzene sulphonyl chloride			
1-naphthalenesulphonyl chloride		(33.088) ^d	
2-naphthalenesulphonyl chloride		(32.584) ^d	

a,b each set of approximately equal intensity

c value reported in reference 9

d weak broad. interactions and weaker following sample purification by vacuum sublimation no corresponding Cl^{37} interactions observed, probably due to impurities and will not be further discussed.

Additionally however at 600 kHz higher frequency there is another similarly intense interaction. The sample failed to yield isomers and the broad features of the spectrum are present at room temperature. By considering 1,3,5-benzenetrisulphonyl chloride it is evident that further substitution barely increases the average frequency. The proximity of the S-Cl³⁵ NQR frequencies of the polysubstituted molecules of Table 9 suggests that the electronic effects of the chloro and fluorosulphonyl and also of the carboxy group, on the benzene system, is similar.

Two difficulties common to the interpretation of solid-state quadrupole coupling data are borne out by the results of Table 9. Firstly, there is evidence of a sometimes large non-bonded contribution to the frequency, as the multiplicity and breadth of the spectra are considerable. Secondly, the practice of comparison and ordering by frequency in different molecules at one temperature, may not apply or may become reversed through observation at another. For quantitative interpretation, knowledge of the magnitude of the asymmetry parameter at chlorine, that is probably considerable and variable in these molecules, is requisite.

Preliminary investigations have indicated widely different NQR frequency temperature dependence coefficients amongst the spectra and also different crystalline phases. Direct comparison of NQR frequencies at one temperature for the low melting point, planar, relatively unsubstituted molecules of the preceding tables is reasonable. Obviously the molecules of Table 9 can and possibly do adopt a variety of conformations in the solid-state resulting in their more complex spectra. This might account for the non-observation of quadrupolar interactions in a further seven similar molecules*.

Both NQR frequency temperature dependence studies and structural information are necessary before worthwhile qualitative evaluations of the spectra of some of these molecules can be made.

* 3 and also 4-fluorosulphonylbenzenesulphonyl chloride, 3-chloroacetylbenzenesulphonyl chloride, 4-carboxylicacidbenzenesulphonyl chloride, 2-chloro, 5-fluorosulphonylbenzenesulphonyl chloride, 4,4-biphenyl-disulphonyl chloride and 8-quinolinesulphonyl chloride.

VI. 4. Summary and Discussion

It has been found possible to account for the range of $S-Cl^{35}$ NQR frequencies of various sulphur atom bonding situations by considering the s-character of the sulphur hybrid orbital to chlorine, together with the sulphur orbital hybridization requirements of the substituents and their total sigma inductive effect.

The frequencies of some arylsulphenyl chlorides studied exhibit no trend identifiable with the electronic nature of the aromatic substituent. In various substituted sulphonyl chloride series, the substituent being other than aryl, the following information was obtained: In the series XSO_2Cl , the frequency shifts parallel the electronegativity of substituent X. For the alkylsulphonyl chloride series the inductive effect experienced by the sulphonyl system due to the alkyl substituent becomes constant once the chain exceeds ethyl. In the N-substituted and also the alkoxy-sulphonyl chloride molecules there is evidence for considerable transmission of inductive effects and conjugative effects are inferred.

In various arylbenzenesulphonyl chloride series the following was found: For the methyl and multimethylbenzenesulphonyl chlorides the observed frequency shifts are adequately explained by considering the inductive effect of the methyl group. In the 4-halobenzenesulphonyl chloride series additional to the inductive effect of the halogen there is evidence of a conjugative effect. In the multichlorobenzenesulphonyl chlorides both inductive and conjugative effects are evident in the S-Cl^{35} NQR frequencies however their C-Cl^{35} NQR frequencies exhibit additive shifts from an inductive effect alone. Explanation of the frequencies of the nitrobenzenesulphonyl chloride molecules requires consideration of strong conjugation of the sulphonyl group with the substituted aromatic system in addition to the inductive effect.

The spectra of the bulky-group substituted benzenesulphonyl chlorides of Table 9 are complicated by the existence of various molecular conformations and phase transitions, to the preclusion of direct qualitative interpretation. The complexity of some of the reported spectra of the few compounds previously studied is found to be due to artifact. These studies have lead to recognition of large scale group reorientation in the trichlorophosphazo and trichloromethane sulphonyl chlorides.

In this attempt to gain information of the chemical bonding of the sulphur atom, the electronic effects of a bonded neighbour were regarded as a perturbation on the electronic structure of this atom, and the quadrupolar nuclei of a bonded chlorine as an indicator of the result. Although the nature of the perturbing substituent was usually a multivariable with respect to the single observable, the chlorine NQR frequency, it proved

possible to determine some of the bonding behaviour of sulphur, from recognition of frequency trends within series of related molecules.

These studies have revealed the sulphur atom to be electronically more "soft" than is carbon, to sigma bond inductive changes. Further the sulphur atom of sulphones in addition to being sensitive to these changes, is perturbed by the conjugative effect. Since one type of electromeric group was found to increase the S-Cl³⁵ NQR frequency and another to reduce this, that is only possible through affecting the extent of $dp\pi$ overlap about this bond, two deductions result: There is a synergic relationship between the π charge density about the bond between the substituent to sulphur and the S-Cl bond. There must be considerable $dp\pi$ overlap between the sulphur and chlorine in many of the compounds studied. This second deduction is of particular significance, for this cannot necessarily be found from direct experiment, by for example NQR Zeeman determination of the asymmetry parameter of this bond, for this is sensitive only to the difference in relative orbital populations along the bond axis.

It is hoped that the results of the studies presented in this chapter may prove useful in calculations, and that this qualitative description will soon be replaced by more precise and definite quantitative interpretation with the advance of molecular orbital theory.

CHAPTER VI

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CHAPTER VII

CHLORINE-35 NUCLEAR QUADRUPOLE RESONANCE INVESTIGATION OF THE N-Cl BOND.

VII. 1. Introduction.

Nuclear quadrupole resonance study of the N-Cl bond yields striking information on the charge density at the chlorine atom due to its similar electronegativity to the atom to which it is bonded. Unfortunately few determinations have been reported, principally due to the instability of N-chloro compounds. The results of a further few are presented here, analysed along with existing literature values, and interpreted within the framework of the LCAO-VB approximation to yield information on the nature of the bonding at the nitrogen atom.

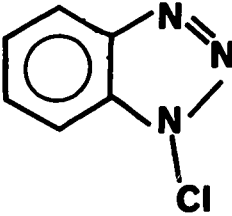
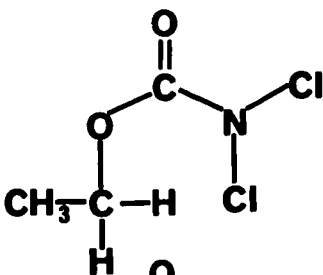
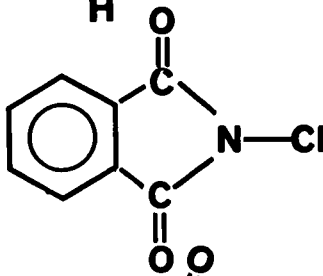
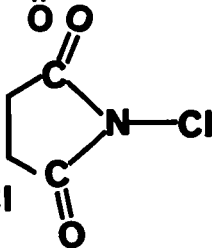
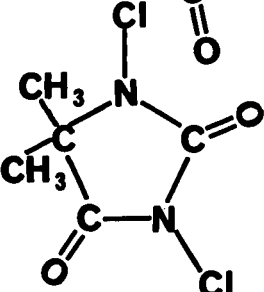
Currently there is available little structural information of N-chloro compounds, this precludes any definite knowledge of the hybrid character of the orbitals at the nitrogen atom. Nevertheless the wide range of observed Cl^{35} NQR frequencies resulting from considerable variation in the charge density at the chlorine atom, can be related to variation in the electronegativity of the nitrogen sigma bond orbital to chlorine and hence rationalized in terms of various hybridization states and the total orbital population.

In N-chloro compounds the nitrogen atom can be understood to exhibit a range of orbital hybridization states from sp^2 through to sp^3 . The extent of hybrid character of the bonding orbitals can be inferred from the molecular geometry and is a function of the neighbouring atoms' bonding orbitals and the total charge available. X-ray structural analysis of the N-chlorosuccinimide molecule¹ has revealed the nitrogen atom and its bonded neighbours to be almost coplanar, with bond angles approximating 120° . Microwave study of nitryl chloride² has indicated a similar situation but its bonding is more complex. Similar investigation of nitrosyl chloride³ and chlorine isocyanate⁴ has indicated that their molecular axes make an angle of about 120° , at the nitrogen. Thus these two molecules can be understood to exemplify a different nitrogen orbital hybridization state, but it might be noted that extreme situations are probably never realized.

VII. 2. Discussion

Table 1 shows the molecules, their nitrogen atom most probable limiting valence state hybridization and Cl^{35} NQR frequencies. The range of observed frequencies can be separated into three regions on the basis of the presumed nitrogen atom orbital hybridization: There is the region above fifty megahertz for chlorine bonded to trigonally hybridized nitrogen with the lone-pair in a π orbital, $tr^1 tr^1 tr^1 \pi^2$. An intermediate region of from forty-four to fifty megahertz is evident, again the chlorine is bonded to trigonal nitrogen, but the lone-pair is in a trigonal orbital, $tr^1 tr^1 tr^2 \pi^1$,

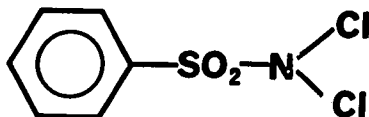
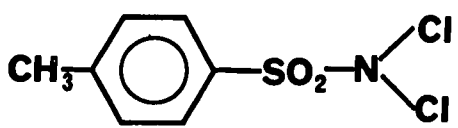
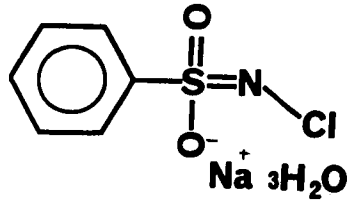
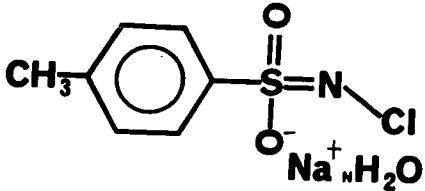
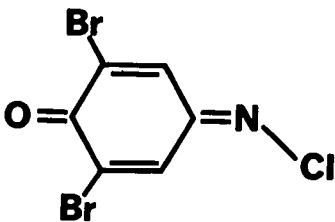
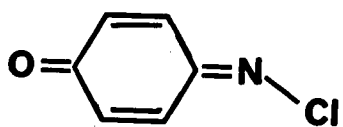
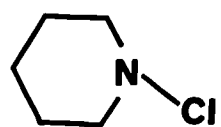
Table 1: Cl^{35} NQR Frequencies^a in MHz of Some N-chloro Compounds at 77°K
and the Nitrogen Atom Most Probable Limiting Valence State
Hybridization and Occupation.

	$\text{tr}^1 \text{tr}^1 \text{tr}^2 \pi^1$ $\text{tr}^1 \text{tr}^1 \text{tr}^2 \pi^1$ $\text{tr}^1 \text{tr}^1 \text{tr}^1 \pi^2$	56.743
1-chlorobenzotriazole		
	$\text{N,N-dichlorourethane}$ $\text{tr}^1 \text{tr}^1 \text{tr}^1 \pi^2$	54.005 ^b 55.591 ^b
	$\text{N-chlorophthalimide}$ $\text{tr}^1 \text{tr}^1 \text{tr}^1 \pi^2$	55.424
	$\text{N-chlorosuccinimide}$ $\text{tr}^1 \text{tr}^1 \text{tr}^1 \pi^2$	54.088 ^c
	$\text{1,3-dichloro-5,5-dimethyl}$ hydantoin $\text{tr}^1 \text{tr}^1 \text{tr}^1 \pi^2$	53.648 ^d 55.962 ^d

^a in each compound, Cl^{37} interaction was observed at the appropriate frequency

^b equal intensity, average frequency 54.798 MHz ^c reported in reference 6 at 54.1 MHz for 77°K ^d equal intensity, lower frequency from chlorine adjacent to methyl group, reported at 53.627 and 55.950 MHz in reference 7.

Table 1 continued:

	"di-chloramine B"	52.254 ^e
	tr ¹ tr ¹ tr ¹ π ²	52.606 ^e
	"di-chloramine T"	51.6 ^f
	tr ¹ tr ¹ tr ¹ π ²	
	"chloramine B"	45.730
	tr ¹ tr ¹ tr ² π ¹	
	"chloramine T"	45.722 ^g
	tr ¹ tr ¹ tr ² π ¹	
	2,6-dibromo-N-chloro- p-benzoquinoneimine	46.306
	tr ¹ tr ¹ tr ² π ¹	
	N-chloro-p-benzoquinoneimine	44.992 ^h
	tr ¹ tr ¹ tr ² π ¹	
	N-chloropiperidine	43.889 ⁱ
	te ¹ te ¹ te ¹ te ²	

^e equal intensity ^f reported in reference 7, no interaction could be detected in samples of this compound. ^g reported at 45.724 in reference. ^h from reference 6. ⁱ from reference 5.

In addition to di-chloramine T, no interactions were detected in the following compounds: 2,6-dichlorobenzoquinoneimine, N,N-dichloro-p-sulphonamidobenzoic acid and its sodium salt, trichloromelamine and N,N',N'',N'''-tetrachloroglycoluril.

that leaves the half-occupied nitrogen π orbital free to overlap with the chlorine and the remainder of the molecule. Finally there is the region below forty-four megahertz represented by the single example of N-chloropiperidine, with the chlorine bonded to nitrogen hybridized viz., $te^1 te^1 te^1 te^2$.

The s-character of the chlorine sigma orbital has been shown independent of the hybridization of the carbon atom to which it is bonded, at about 20%, however the ionic character is understood to vary considerably⁸. The same study applied to N-chloropiperidine, with the assumption of no π bonding, indicated 12% s-character and 10% ionic character for the chlorine orbital bonded to nitrogen. In the C-Cl bond the change from carbon $te^1 te^1 te^1 te^1$ to $tr^1 tr^1 tr^1 \pi^1$ involves a 6% decrease of ionic character with constant s-character and little variation in π bonding⁹. Assuming that the N-Cl bond behaves likewise, in going from N-chloropiperidine to the N-chloro-p-benzoquinoneimines and the partial chloramine salts, (Table 1), similar change in ionic character would result in a Cl^{35} NQR frequency increase of about three megahertz, that is about the centre of the intermediate frequency region already recognized.

The further Cl^{35} NQR frequency increase observed amongst these molecules in going from nitrogen inferred $tr^1 tr^1 tr^2 \pi^1$ to $tr^1 tr^1 tr^1 \pi^2$ reflects an additional decrease of chlorine sigma orbital ionic character. This is due to two effects: a considerable reduction in the π character of the N-Cl bond and an increase in the total sigma bond inductive effect at nitrogen. The former is the result of the nitrogen π orbital becoming

filled and the latter because of the nitrogen π orbital, that previously contained the lone-pair, becoming sigma bonding to a second highly inductive atom, that is in every compound here chlorine.

The BEEM- π method that has been fully described⁹ has been applied to the amenable molecules of Table 1 to predict their N-Cl bond characters. In applying this method it is necessary to assume the hybridization at the nitrogen atom and also that the 12% chlorine orbital s-character found for N-chloropiperidine applies generally to N-chloro compounds. The predicted orbital populations are substituted into the Townes-Dailey expression, (Chapter I-5), to yield a predicted value for the Cl^{35} NQR frequency and bond asymmetry parameter. The results are set out in Table 2.

The magnitudes of the predicted asymmetry parameters are heavily dependent on the π system input parameters as are also the frequencies, but to a lesser extent. The empirical α and β parameters associated with each atom or bond had to be found for inclusion of the heteroatoms into the Hückel molecular orbital section of the computation. These are incorporated into the machine program in units of standard α_o and β_o by use of the following definitions;

$$\alpha_x = \alpha_o + h_x \beta_o,$$

$$\beta_{cx} = k_{cx} \beta_o.$$

The h and k parameters, representing the coulomb and resonance integrals respectively, for the heteroatom x , relative to carbon, were taken from

Table 2

Results of BEEM- π Calculations of some N-Cl³⁵ Bonds Assuming 12% s-Character in the Chlorine σ -Orbital

	occupancy of Cl σ -orb. in e's	occupancy of Cl π -orb. in e's	predicted η %	predicted ν res.MHz	% different from expt.
N-chloropiperidine	1.095	2.0000 ^a	(a)	(45.552)	(a)
N-chloro-p-benzo- quinoneimine	0.99011	1.83142	15.7	44.322	-1.49
N-chlorophthalimide	0.86407	1.99098	0.7	54.605	-1.48
N-chlorosuccimide	0.84590	1.98850	0.9	55.414	+2.45
N,N-dichlorourethane ^b	0.80496	(1.92973) ^b	(5.2) ^b	55.803	+1.83 ^c
1,3-dichloro-5,5-dimethyl hydantoin	0.89466	1.99339	0.5	53.194	-1.51
	0.85419	1.98985	0.8	55.051	-0.98
1-chlorobenzotriazole	0.89102	1.99317	0.5	53.363	-5.96

^a assumed. ^b excluding the ethoxy oxygen in the π system due to computational difficulties.

^c from the average of the observed Cl³⁵ NQR frequencies.

the standard text¹⁰ and in some cases very slightly modified for the above purpose. In the absence of literature values, those determined in this laboratory were used. All the values employed in the determination of the results of Table 2 are listed in Table 3. Use of values that have been employed in this laboratory for N¹⁴ NQR prediction led to three-fold better agreement between prediction and experiment. Since these parameters lack any theoretical basis, but probably merely accomodate imperfections in the computational method they shall not be discussed.

Table 3. Parameters Employed for Heteroatom Inclusion in the Huckel Molecular Orbital Part of the BEEM- π Predictions Listed in Tables 2 and 4.

Element	Bond	Coulomb Integral	Bond Integral
C	C=C	0.0	1.0
	C=O	0.2	0.9
$\dot{\text{O}}$	O=N	1.0	0.7
$\ddot{\text{O}}$	O-C	1.0	0.8
$\ddot{\text{N}}$	N-Cl	1.5	0.7
$\dot{\text{N}}$	N-C		0.8
	N-N		0.5
	N-Cl	0.56	1.2
	N-C		0.8
	N=C		1.0
^+N	N=N		1.8
	nitro	2.0	0.7
Cl		2.0	

The calculations were tested against the chlorine quadrupole coupling information from the microwave studies of three molecules that are the only N-chloro compounds of known geometry and N-Cl³⁵ bond asymmetry parameter. The results of this application of the calculations are listed in Table 4 and are quite poor. This outcome might be mitigated by the realization that the BEEM- π method was developed to yield good solid-state bond information and it is to be noted that the determined geometries of these molecules depart from ideality. Further their observed quadrupole coupling results depend heavily on precise transformation of the coefficients from the principal inertial axial system of the molecule to the presumed direction of the principal axis of the electric field gradient of the N-Cl bond. In the case of nitryl chloride no transformation is necessary however its nitrogen valence shell orbital hybridization is rather complex for the BEEM- π method to be applied with confidence.

VII.3. Discussion of the Results

In Table 2 it can be seen that the predicted Cl³⁵ NQR frequencies tend to be lower than those observed. The asymmetry parameters are of significance. Concomitant with its presumed hybridization state, N-chloro-p-benzoquinoneimine is predicted to have an asymmetry parameter of 15.7%. Unfortunately the computational method cannot be applied to 2,6-dibromo-N-chloro-p-benzoquinoneimine. The N-Cl³⁵ NQR frequency of this molecule occurs at 1.3 MHz higher frequency than that of the parent molecule as a result of the transmission of the inductive effect due to 2,6-dibromo substitution. Over the temperature range 77 to 294°K its Cl³⁵ NQR frequency

Table 4

BEEM- π Predictions of Cl³⁵ Quadrupole Coupling and N-Cl Bond Character of Three Gases Studied by

Microwave Spectroscopy.

	Cl-N-X angle deg.	occupancy of Cl σ -orb.in e's	occupancy of Cl π -orb. in e's	predicted e^2Qq MHz	experimental e^2Qq MHz	predicted η %	experimental η %
nitrosyl- chloride ^a NOCl tr ¹ tr ¹ tr ² _{π} ¹	113	1.02406	1.74933	80.498	-63.4	25.6	32.5
nitryl- chloride ^b NO ₂ Cl tr ¹ tr ¹ tr ¹ _{π} ²	115	0.97013	1.76754	86.705	-96.8	22.1	8.7
chlorine isocyanate ^c Cl NCO tr ¹ tr ¹ tr ² _{π} ¹	123	1.01238	1.79442	84.100	-118.3	20.1	4.1

^a reference 2

^b experimental values are the average of two studies, reference 3

^c reference 4.

has an apparent temperature coefficient of only $-68 \times 10^{-6} \text{ deg}^{-1}$. Typically this coefficient has a value of about $-130 \times 10^{-6} \text{ deg}^{-1}$ for a covalently bonded chlorine atom and low values have been interpreted¹¹ as indicating reduction of π bonding with increasing temperature. It is likely that such a process is effective in this molecule. Conceivably the amplitudes of the oscillations away from the plane of the delocalized charge increase with temperature reducing π overlap about the N-Cl bond and thus augment the chlorine sigma orbital relative electron deficit. Thus the apparent temperature coefficient is taken as indicating considerable N-Cl π bonding in 2,6-dibromo-N-chloro-p-benzoquinoneimine.

The chlorine sigma orbital occupancy of the N-chloroimides, (Table 2), is interesting. It indicates that their N-Cl bonds have negative ionic characters in accordance with the concept of the rôle of these compounds in organic chemistry as being sources of "positive chlorine", or effecting radical chlorination. Since their predicted asymmetry parameters are vanishingly small, to be expected for their presumed nitrogen atom hybridization state, the N-Cl linkage is virtually a pure covalent bond.

The higher Cl^{35} NQR frequency observed for N-chlorophthalimide compared to that of N-chlorosuccinimide at the same temperature is the result of inclusion of the saturated carbon atoms of the latter, as part of a delocalized charge system. In N-chlorosuccinimide the carbonyl groups exert both a sigma and π inductive effect on the chlorine through the nitrogen, whereas in N-chlorophthalimide the carbonyl can also be in conjugation with the aromatic system reducing the demand on the chlorines, hence the

observed higher frequency for the latter molecule. Although this argument is sustained by the predicted asymmetry parameter of N-chlorosuccinimide exceeding that of N-chlorophthalimide, the sigma orbital occupancies are in reverse order to that suggested by the observed Cl^{35} NQR frequencies.

These calculations enable assignment of the pair of observed Cl^{35} interactions of 1,3-dichloro-5,5-dimethyl hydantoin to their respective nitrogen atoms. The higher frequency interaction results from the N-Cl bond between the two carbonyl groups and the lower from the chlorine on the nitrogen adjacent to the carbon with the two methyl groups. Apparently the sigma bond inductive effect of the dimethyl carbon moiety is less than that of the carbonyl unit. For the chlorine adjacent to the methyl carrying carbon, there is less π inductive effect through its nitrogen, than for the chlorine of the nitrogen between the two carbonyl groups. This is indicated by the predicted lower asymmetry parameter for the former chlorine whereas that of the latter is equal to that of the other N-chloroimides.

The observed Cl^{35} NQR frequency of 1-chlorobenzotriazole is at the extreme for the N-chloromolecules of the solid-state. This indicates the considerable sigma bond inductive effect exerted by the triazole or three heteroatom system. The predicted frequency result reflects heavily the use of inappropriate Hückel parameters. If the predicted asymmetry parameter is meaningful, its small value indicates the presence of only a low π inductive effect.

The four N-chlorosulphonamido compounds, although all presumed to have a trigonally hybridized nitrogen atom, exhibit considerable Cl^{35} NQR frequency difference. The electronic structures for the two partial salts, shown in Table 1, are the only reasonable representations. On such a basis their frequency difference is reasonable. In the chloramines, unlike the dichloramines, the lone-pair is contained in a trigonal orbital, thus there is a greater total orbital population on the nitrogen and further only one instead of two chlorines competing for the available charge. Therefore the N-Cl bond of the chloramines has a greater ionic character and there will also be π overlap resulting in their lower Cl^{35} NQR frequency. The presence of the cation need not be considered to have a significant contribution to the electric field gradient of such covalently bound atoms.

In both pairs of chloramines the paramethyl substituted molecule has the lower Cl^{35} NQR frequency. This is consistent with the observed effect of the para-methyl group of 4-methylbenzenesulphonyl chloride, in which the Cl^{35} NQR occurs at lower frequency than that of benzenesulphonyl chloride and is discussed in Chapter VI of this Thesis. Apparently the ability of the sulphone unit to transmit inductive effects originating within the aromatic system is also possessed by the sulphonamido unit.

The average of the Cl^{35} NQR frequency of N,N-dichlorourethane is 4% greater than that of dichloramine B for the same temperature. Comparison of the Cl^{35} NQR frequencies of an analogous pair of molecules, ethylchloroformate, $\text{C}_2\text{H}_5\text{OCOC}\text{Cl}$, (Chapter VIII of this Thesis), and benzenesulphonyl chloride also indicates that the molecule with the sulphone system has a lower chlorine NQR frequency, in this case of about 6%.

In either case the presence of the sulphone system could lead to considerable delocalization of charge from the lone-pair chlorine orbitals and this process would contribute to the lower frequencies observed. There is no experimental evidence for this process in such molecules however the interatomic distances from the X-ray structural determination of ethyl carbamate (urethane)¹² indicate considerable charge delocalization between the carbonyl system and the ethoxy oxygen, and that the C-N linkage is very nearly a single bond. If the bond character of the C-N linkage in N,N-dichlorourethane is similar to that of urethane then some of the reduced Cl^{35} NQR frequency of the dichloramines with respect to that of N,N-dichlorourethane can be related to π character in their N-Cl bond.

The high Cl^{35} NQR frequency of N,N-dichlorourethane is due to the considerable inductive effect of the two chlorines competing for the charge at the nitrogen. The BEEM- π frequency prediction is poor principally due to the inapplicability of the method to the situation of an ether linkage adjacent to a delocalized charge system*. Probably the π character of the N-Cl bond is less than the calculation indicates, for the chlorine π orbital occupancy is too low because of the neglect of the π -charge contribution of the ethoxy oxygen that would otherwise satisfy the π inductive effect of the carbonyl system.

The presence of a 1.6 MHz difference in the two Cl^{35} NQR frequencies of N,N-dichlorourethane reflects inequivalence of the chlorines. If the NCl_2 group was not orientated perpendicularly and equally about the plane of the remainder of the molecule, then such a

*This is due to the difficulties of parameterization for this oxygen.

difference would constitute chemical inequivalence. Of course any N-Cl π bond character requires the molecule to be planar. Intermolecular interactions that would result in physical inequivalence at the chlorine sites do not present an adequate explanation of the frequency difference in view of the low (circa-100°C) melting point of this compound. Whereas in urethane, that has a melting point about 50°C, extensive intermolecular hydrogen bonding has been revealed by the X-ray structural analysis¹². To account for the 1.6 MHz Cl³⁵ frequency difference of the two interactions of N,N-dichlorourethane it is reasonable to postulate intramolecular interaction between the lower frequency chlorine and a hydrogen of the methylene group, that would result in the formation of a six membered cyclic system.

VII. 4. Conclusion.

It is possible to interpret the Cl³⁵ NQR frequencies of these N-chloro molecules in terms of inductive and conjugative effects in the N-Cl bond and thereby rationalize the results against various possible orbital hybridization states of the nitrogen atom within the LCAO-VB approximation. While these possible hybridization states are rather arbitrarily chosen, only in compliance with the presumed molecular geometry and are more definite than the intermediate condition more probably realized, at least they are quite consistent and complementary with the experimental results and are strongly supported by the calculations whenever applicable.

CHAPTER VII.References

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CHAPTER VIII

CHLORINE-35 NQR OBSERVATIONS ON THE ACYL CHLORINE OF ALKYL CHLOROFORMATES, ALKYL ACID CHLORIDES AND CARBAMYL CHLORIDES

The electronic structure of the chlorocarbonyl group is of interest as the recognized planarity^{1,2} of the $-X-C(=O)Cl$ system implies the presence of delocalized charge. The aim of the studies of this Chapter was to compare the relative effects of atoms of varying π -bonding ability on this group, through observation of the chlorine NQR frequency of pairs of molecules of X being oxygen and sulphur, i.e., chloroformates and thiolchloroformates. Unfortunately none of the sulphur containing analogues gave quadrupolar interactions. Similarly no comparison could be made between the carbamyl and thiocarbamyl chlorides. As frequency variation was recognized among the results of some chloroformates, their acid chloride analogues were examined in an endeavour to determine the role of the ether oxygen in transmitting inductive effects. Eventually results were obtained for thirteen pairs of molecules similar in R; $ROC(=O)Cl$ and $RC(=O)Cl$. As the frequency differences within each series are small, intercomparison by pairing exhibits only randomness when plotted. In the absence of calculations capable of reproducing these small frequency differences, only brief qualitative discussion is presented. The series of molecules studied are merely representative and not exhaustive.

Single temperature frequency comparison within a series of molecules presumes at least a constant geometry of the group containing the

quadrupolar atom. Unfortunately for some chloroformates, cyclic formulations as dioxans³ have been postulated. In the Literature there appears conflict in the interpretation of the structure of the chloro and thiolchloroformates. For example methylchloroformate is considered for both the liquid and gas phases to have the methyl ester group cis to the carbonyl oxygen atom¹ whereas another report⁴ states that the preferred configuration of both types of esters is the halogen atom and the hydrocarbon group cis to each other. For ethylchloroformate, the only example studied⁶, a single Cl³⁵ NQR frequency is reported, see Table 1. However in all the samples of this compound examined, from a variety of conditions, a pair of interactions at a more reasonable frequency was always observed. As an example of potential complexity in the acid chloride series, a recent vibrational spectral study of fluoroacetylchloride comments that only after annealing will the solid sample be of entirely the lowest energy conformation⁶. Similarly for chloroacetylchloride the presence of solid-state isomers is mentioned⁷.

VIII.1. The Chloroformate Molecules

Listed in Table 1 are the Cl³⁵ NQR frequencies of some chloroformates. The frequencies of the n-alkyl molecules are almost constant for the ester unit exceeding two carbon atoms. Even separation of the phenyl group from the chloroformate system by a single methylene unit quenches its apparent inductive effect. The acyl chlorine frequencies of 3-chloropropyl, allyl and ethylene glycol bis(chloroformate) in exceeding this constant value, indicate that the chlorocarbonyl group can

Table 1. Cl^{35} NQR Frequencies in MHz of Some Chloroformates at 77°K

	acyl chlorine	carbon chlorine		
$(\text{CF}_3)_3\text{COCOC1}$	36.737			
$\text{C}_2\text{F}_5\text{OCOC1}$	36.563		36.731	
$i\text{-C}_3\text{F}_7\text{OCOC1}$	36.258			
$\text{F}_5\text{SOCOC1}$	36.604			
$\text{Cl}_3\text{CCH}_2\text{OCOC1}$	35.691	38.746	38.918	39.141
$\text{ClCH}_2\text{CH}_2\text{OCOC1}$	34.436 ^a		34.319 ^a	
$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{OCOC1}$	34.194 and 33.968,		33.370 and 33.069	
$\text{CH}_2=\text{CHCH}_2\text{OCOC1}$	34.282			
$\text{C}_6\text{H}_5\text{OCOC1}$	34.818			
$p\text{-CH}_3\text{OC}_6\text{H}_4\text{OCOC1}$	34.943			
$\text{C}_6\text{H}_5\text{CH}_2\text{OCOC1}$	33.772			
$\text{CH}_3\text{OCOC1}$	34.257			
$\text{C}_2\text{H}_5\text{OCOC1}$	34.270 and 34.364	(33.858) ^b		
$n\text{-C}_3\text{H}_7\text{OCOC1}$	33.823			
$n\text{-C}_4\text{H}_9\text{OCOC1}$	33.746			
$n\text{-C}_5\text{H}_{11}\text{OCOC1}$	33.770			
$n\text{-C}_6\text{H}_{13}\text{OCOC1}$	33.749			
$n\text{-C}_7\text{H}_{15}\text{OCOC1}$	33.806			
$n\text{-C}_8\text{H}_{17}\text{OCOC1}$	33.873			
$(\text{CH}_3)_2\text{CHOCOC1}$	33.798 and 33.701			
$(\text{CH}_3)_2\text{CHCH}_2\text{OCOC1}$	34.030 and 34.082			
$\text{O}-(\text{CH}_2\text{CH}_2\text{OCOC1})_2$	34.102 and 34.848			

^a these assignments are arbitrary. ^b from reference 5. attempts to crystallize samples of $(\text{CH}_2\text{OCOC1})_2$ were fruitless. all multiple interactions are of equal intensity, no interactions were detected in $\text{CF}_3\text{OCOC1}$ or $\text{CH}_3(\text{CF}_3)_2\text{COCOC1}$.

experience inductive charge effects transmitted over the ethylene unit. Of the four perfluoromolecules, the Cl^{35} NQR frequency of pentafluoro-sulphurchloroformate is high, for although the inductive effect of the substituent group will be considerable, back-bonding through the sulphur d-orbitals would be expected to lead to reduction. It is no surprise that perfluorotertiarybutylchloroformate exhibits the highest Cl^{35} NQR frequency of the series.

To predict how the ester or perfluoroester substituent affects the charge in the chlorocarbonyl group is a major task. Apparently in methylchloroformate the carbonyl linkage is shortened from that usually observed and the $\text{O}\hat{\text{C}}\text{O}$ angle exceeds the classical value¹. This might be interpreted as indicating multiple bond character involving the ether oxygen lone-pairs. Curiously, the alkoxyl linkage appears to be lengthened⁴. The π -orbital population of the etheroxygen is unlikely to be independent of the sigma bond orbital population variation from substituent effects. Consequently even the purely inductive substituents will modify both the sigma and π -electron density of the chlorocarbonyl group, the aggregate of this becomes reflected in the chlorine NQR frequency variation.

VIII. 2. The Acid Chloride Molecules

The Cl^{35} NQR frequencies of some acid chlorides listed in Table 2 extend over a considerable range. Although in the n-alkaloyl series there is no evidence of substituent effects, the chlorocarbonyl group appears sensitive to the nature of the substituent. The tertiarybutyl

group of pivaloylchloride confers this molecule the distinction of having the lowest C-Cl³⁵ NQR frequency observed, some five megahertz below the acyl-chlorine frequency of the perhalo molecules of Table 2. The reported⁸ result for chlorocarbonylchloride appears unreasonably high. It is surprising that the single chlorine substituent appears to result in an almost two and one-half megahertz frequency increase over the perhalo groups on the chlorocarbonyl system. The acyl-chlorine frequencies are all close in the trihaloacetylchloride molecules irrespective of the halogen atoms. In a sample of chlorodifluoroacetylchloride only one Cl³⁵ interaction was apparent. Another about forty megahertz is to be expected. It is tempting to attribute its non-observation to re-orientational effects in the trihalomethyl group. Interestingly the trifluoroacetyl molecule is at lower frequency than the trichloroacetyl one, similar reversals have been observed and discussed in the halomethane series¹². It appears from considering both the frequencies of both 3-chlorobutyrylchloride and 2-chloropropionylchloride that sigma bond inductive effects are not transmitted beyond the ethylene unit. The benzoylchloride frequency value is one megahertz above the constant value of the n-alkaloylchlorides, paramethoxy substitution appears to result in loss of this increase. In the benzenesulphonyl chlorides discussed in Chapter VI of this Thesis, this group was observed to have no effect on the frequency. Apparently sigma bond inductive effects are transmitted about the pyridine system considering the elevated frequency observed for the pyridine-2,6-dicarboxylicacid-chloride molecule.

The SGOBE method¹³ of orbital electronegativity equalization has been employed to estimate charge densities in non-conjugated molecules.

Table 2 NQR Frequencies in MHz of some Carboxylic Acid Chlorides at 77°K

	acyl chlorine	non-acyl chlorines	
ClCOCl	(35.081, 36.225) ^a		
$\text{Cl}_3\text{CCOCl}^b$	33.721	40.132, 40.473	40.613
$n\text{-C}_3\text{F}_7\text{COCl}$	33.753		
$\text{C}_2\text{F}_5\text{COCl}$	33.412		
CF_3COCl^f	33.438		
$\text{CClF}_2\text{COCl}^f$	33.444	(---) ^e	
$\text{CCl}_2\text{HCOCl}^c$	32.147, 32.962	38.353, 38.521	39.189, 39.386
$\text{CClH}_2\text{COCl}^c$	30.437	37.517	
CBrH_2COCl	30.452		
$\text{ClCH}_2\text{CH}_2\text{COCl}$	29.471	34.018	
$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{COCl}$	29.027	32.875	
$\text{C}_6\text{H}_5\text{COCl}$	29.914 ^d		
$p\text{-CH}_3\text{OC}_6\text{H}_4\text{COCl}$	28.949		
CH_3COCl	28.909, 29.079		
$\text{C}_2\text{H}_5\text{COCl}$	29.138		
$n\text{-C}_3\text{H}_7\text{COCl}$	29.004		
$n\text{-C}_5\text{H}_{11}\text{COCl}$	28.991		
$n\text{-C}_6\text{H}_{13}\text{COCl}$	29.084, 29.150		
$n\text{-C}_7\text{H}_{15}\text{COCl}$	29.067		
$(\text{CH}_3)_2\text{CHCOCl}$	28.950	(iso-butyrylchloride)	
$(\text{CH}_3)_2\text{CHCH}_2\text{COCl}$	28.807	(iso-valerylchloride)	
$(\text{CH}_3)_3\text{CCOCl}$	28.355	(pivaloylchloride)	
$\text{CH}_2=\text{CHCOCl}$	29.954, 30.124	(acryloylchloride)	
$\text{CH}_3\text{CH}=\text{CHCOCl}$	29.482	(crotonylchloride)	
$\text{ClCH}=\text{C}(\text{Cl})\text{COCl}^f$	32.482, 32.517	36.001 ^g , 36.092 ^g	37.609 ^h , 37.872 ^h
$\text{CH}_3\text{OC}(\text{O})\text{COCl}$	31.929	(ethylchloro oxylate)	
$\text{N}-(\text{C}(\text{COCl})\text{CH}_2\text{CH}_2)_2^f$	31.454, 31.892	(pyridine-2,6-dicarboxylicacidchloride)	
$\text{ClSO}_2\text{CH}_2\text{COCl}$	31.973, 32.501	(34.951, 35.191)	

all multiple interactions are of equal intensity. ^a from reference 8 see text.

^b from reference 9. ^c from reference 10. ^d reported¹¹ at 29.93 MHz. ^e see text.

^f very broad interactions. ^g α -C-Cl bond. ^h β -C-Cl bond. No quadrupolar interactions were detected in methylchloro-oxylate; valeryl, cinnamoyl or itaconyl chloride.

The variation in group electronegativity is identified with the nature of the complementary group that together define the direction of flow of charge density. Charge densities from the electronegativity equalization method have been employed in the analysis of the transmission of inductive effects through localized carbon-carbon bonds of hydrocarbons¹⁴. It proved possible to define the magnitude of the inductive effect along the alkyl chain with length increase. Complete damping was recognized at the fourth carbon atom. This observation, along with the SGOBE prediction of the direction of charge flow, together are in accordance with the trend apparent in the n-alkylchloroformate series. The n-alkaloylchlorides appear to be at variance. The Cl^{35} NQR frequencies of both acetyl and propionylchloride are already equal to the constant value of twenty-nine megahertz of n-butyrylchloride.

By similar methods the relative electronegativity at the carbon atom, for a tertiary over a secondary carbon, etc., through to the proton, has been established¹⁴. Along with the SGOBE consideration this accounts for the particularly low frequency observed for pivaloylchloride. It has also been found and shown that the electronegativity of a singly-occupied carbon s-p hybrid orbital increases linearly with the extent of s-orbital character¹⁴. Thus the replacement of a carbon-carbon single bond of an alkyl chain by either a double or triple bond will result in charge density displacement toward the unsaturated bond. Apparently this effect is experienced in the chlorocarbonyl system in view of the elevated Cl^{35} NQR frequencies of the acryloyl and crotonylchlorides with respect to their n-alkyl analogues.

Intercomparison of the two series is now in order. The overall frequency range exhibited by the chloroformate series is less than that exhibited by the acid chlorides. The ester oxygen of the former is probably effective in diminishing the sigma-bond inductive effects of the substituent. However, whereas the n-alkylchloroformates exhibit a small frequency variation with increase in chain length, the n-alkaloylchlorides exhibit none. In the latter series, substitution is through the carbonyl carbon and in the former, via the ester oxygen, that also can be in conjugation with the chlorocarbonyl system. No explanation of the apparent difference will be attempted, for detailed calculations are necessary. It is the n-alkaloyl series that appears anomalous.

It can be noted that paramethoxy substitution in the chloroformate series results in no frequency decrease, as was observed in the benzenesulphonyl chloride series and contrary to that observed for the benzoylchlorides. On the basis of the explanation of the low frequency of pivaloylchloride it is reasonable that perfluorotertiarybutylchloroformate presents the other extreme. It will be interesting to examine their triethyl and trityl analogues, that should amplify their observed frequency trends.

VIII.3. Chlorine in the Thiocarbonyl System.

It has already been mentioned that the purpose of these studies was to investigate the relative effects of oxygen and sulphur on the charge distribution of the chlorocarbonyl system, however the thiolchloroformates failed to yield quadrupolar interactions. Interactions were

observed in one dithiocarbonylchloride and also in one oxythiocarbonylchloride molecule studied so this system will be discussed briefly. The key molecule for qualitative comparison is thiocarbonylchloride, however no result could be found at 77°K. If its crystal structure is any more complicated than that observed for carbonyl chloride¹⁵, that is remarkable in yielding the reported and anomalously high quadrupolar interactions, then this non-observation is reasonable.

The molecules and their Cl^{35} NQR frequencies in MHz at 77°K are:

p-chlorophenyldithiocarbonylchloride	$\text{ClC}_6\text{H}_4\text{SC(S)Cl}$	34.284 ⁺ 35.443
phenoxythiocarbonylchloride	$\text{C}_6\text{H}_5\text{OC(S)Cl}$	35.825
phenylchloroformate (for comparison)	$\text{C}_6\text{H}_5\text{OC(O)Cl}$	34.818

(+ This interaction is assigned to the aromatic chlorine).

Of the latter two of the three molecules above, the one with the thiocarbonyl group is at one megahertz higher frequency. This is another example in contradiction to the respective position of sulphur in the atomic electronegativity scale. Such an observation, twice previously in this Thesis, has been rationalized against possible d-orbital involvement. Apparently the sulphur atom is exerting an overall enhanced inductive effect, that is experienced by the chlorine. How sulphur d-orbital participation might effect this is unclear. Irrespective of the validity of the assignment in the dithio molecule, its carbonyl chloride is at lower frequency in comparison with the result of the phenoxythiocarbonyl molecule. This might be identified with the presence of the thiol linkage, that would facilitate charge release from the phenyl group into the thiocarbonyl system more

effectively then would the ester oxygen of the latter molecule. Speculation on these interesting results is better restrained in anticipation of calculations.

VIII. 4. Chlorine in the Carbamyl System

Five carbamylchloride compounds were examined see Table 3.

Table 3. The Cl^{35} NQR Frequencies in MHz of Some Carbamyl Chlorides at 77°K

dimethylcarbamylchloride	$(\text{CH}_3)_2\text{NCOC1}$	31.909
diethylcarbamylchloride	$(\text{C}_2\text{H}_5)_2\text{NCOC1}$	31.879 ⁺
diphenylcarbamylchloride	$(\text{C}_6\text{H}_5)_2\text{NCOC1}$	33.202
methylphenylcarbamylchloride	$(\text{CH}_3)(\text{C}_6\text{H}_5)\text{NCOC1}$	32.664
ethylphenylcarbamylchloride	$(\text{C}_2\text{H}_5)(\text{C}_6\text{H}_5)\text{NCOC1}$	32.951

+ at 2 kHz higher frequency than reported in reference 12.

The unsymmetrically substituted two molecules gave intense Cl^{35} quadrupolar interactions that exhibited apparently normal temperature dependence on which checks were made due to the current interest in C-N bond reorientation^{16,17}. Onset of this in the solid-state would be manifested by the NQR frequency and line width behaviour. The Cl^{35} NQR of the diphenyl molecule is particularly feeble. Samples of dimethyl and diethylcarbamylchlorides were also examined. Unfortunately, despite purification to water white crystals, no interactions were detected.

The molecules and their determined Cl^{35} NQR frequencies are listed in Table 3. The apparent trend in the frequencies of the symmetrically substituted three is reasonable. It is completely in accord with the predictions on sigma-bond inductive effects, discussed in VIII.2, from electronegativity calculations and including the phenyl group. Further the average of these inductive effects is manifested in the frequencies of the two unsymmetrically substituted molecules, for these rank intermediate between the values of their respective symmetrically substituted congeners. Apparently the trigonally hybridized nitrogen atom of the carbamyl system is effective in transmitting inductive effects in these assumed planar molecules.

In conclusion it can be stated that although the initial aim of the studies of this chapter was completely frustrated by the non-observation of quadrupolar interactions in any of the relevant sulphur molecular analogues⁺, these results are easily and profitably rationalized on simple sigma-bond inductive considerations. However, in the chlorocarbonyl system, this effect is not simply indicated by the chlorine charge probe, for obviously it also affects the delocalized charge system of the group. The only precise experimental determination of π -bonding in the acyl carbon-chlorine is the microwave analysis of acetylchloride that indicated $(9.3 \pm 3)\%$ double-bond character². Again it is hoped that the results presented in this chapter will find application in the development of molecular-orbital calculations.

⁺ The compounds are: methyl, ethyl, n-propyl and n-octylthiolchloroformate.

CHAPTER VIII

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APPENDIX

1. Organic Molecules

To provide data for application of intended modifications to BEEM- π some compounds were examined having chlorine bonded into systems of delocalized charge. Their chlorine NQR frequencies are listed in Table 1. On these and other molecules also listed brief comment will be made.

Dichlorodicyanomethane (dichloromalonitrile) with Cl^{35} NQR frequencies about 43.45 MHz supersedes chlorotrinitromethane by half a megahertz as the molecule with the highest C-Cl^{35} NQR frequency¹. This is obvious evidence of the considerable sigma-bond inductive effect of the nitrile group. Chlorocyanoform², $\text{C(CN)}_3\text{Cl}$, another pseudo-halogen can be expected to exhibit an even higher frequency. The six megahertz frequency drop to that of 2-chloroacrylonitrile, (Table 1), illustrates the relative charge releasing ability of the vinyl grouping. Unfortunately a small sample of tricyanovinyl chloride failed to indicate any interactions.

The one megahertz difference in the frequency of the two interactions observed for phenylisocyanide dichloride can be taken as evidence of $\text{tr}^1\text{tr}^1\text{tr}^2\pi^1$ orbital hybridization at nitrogen and it is therefore due to chemical inequivalence. Samples of its chloro-substituted analogue, p-chlorophenylimidocarbonyl-chloride yielded no interactions. The nitrogen orbital hybridization of dichloroglyoxime will be similar and the proximity of its Cl^{35} NQR frequencies precludes the presence of more than one isomer in the sample studied at 77°K. In previous Chapters of this Thesis a high

Table 1: Some Compounds, Their Line Formulae and Cl^{35} NQR

Frequencies at 77°K^a

dichlorodicyano methane	$\text{Cl}_2\text{C}(\text{CN})_2$	43.308 43.604
2-chloroacrylonitrile	$\text{CH}_2=\text{C}(\text{Cl})\text{CN}$	37.677
phenylisocyanide dichloride	$\text{C}_6\text{H}_5\text{N}=\text{CCl}_2$	36.128 37.047
dichloroglyoxime	$\text{HON}=\text{C}(\text{Cl})-\text{C}(\text{Cl})=\text{NOH}$	37.136 37.184
trichloroacetylisocyanide	$\text{Cl}_3\text{C}(\text{O})\text{NCO}$	39.706 39.876 40.795
mucochloric acid ^b	$\text{CHOC}(\text{Cl})=\text{C}(\text{Cl})\text{COOH}$	36.578 36.625 37.336
chloranilic acid	$\text{C}_6\text{Cl}_2\text{O}_2(\text{OH})_2$	37.145
chloranilic acid barium salt	$\text{C}_6\text{Cl}_2\text{BaO}_4$	34.483 34.701
chloranilic acid disodium salt	$\text{C}_6\text{Cl}_2\text{Na}_2\text{O}_4$	34.853 35.538
2,3-dichloro-5,6-dicyano-1,4-benzoquinone		38.335 38.338
	298°K: 37.694	77°K: 38.375
	37.811	38.378
dimethyltetrachloroterephthalate	$\text{C}_6\text{Cl}_4-1,4-(\text{COOCH}_3)_2$	35.762
	298°K: 36.831	77°K: 37.466
	36.950	37.530
	37.095	37.577
	37.383	

^a every interaction of each chlorine isotope is of equal intensity for that compound

^b apparently erroneously reported in reference 4 .

sigma-bond inductive effect was recognized in the isocyanate group. Possibly this is not transmitted by the adjacent oxygen in trichloroacetyl-isocyanate, for its Cl^{35} NQR frequencies are not particularly high compared to those typically observed for the trichloromethyl group³.

The three interactions listed in Table 1 observed in mucochloric acid are interesting. Only two were observed about the same frequency for that temperature, according to a report⁴. This was possibly due to inability to resolve the spectrum. The same three interaction Cl^{35} spectrum persists at room temperature although the line-widths are greatly reduced, thus over-ruling the likelihood its origin from the superposition of the spectra of isomers. Eight different cis and trans isomers are conceivable however the molecular formulation of 3,4-dichloro-5-hydroxy-2-oxo-2,5-dihydrofuran is clearly not sustained by the observation of three interactions of equal intensity. The possible effects of varying the sample crystallinity were not investigated.

The Cl^{35} NQR of chloranilic acid (2,5-dichloro-3,6-dihydroxy-p-benzoquinone) of Table 1 is about 400 kHz lower than that of the average of chloranil, (tetrachloro-p-benzoquinone) at the same temperature⁵. The decrease can be related to substitution of two chlorine atoms of the latter with hydroxyl groups in the former, that are of slightly less electronegativity. The considerable frequency reduction observed from chloranilic acid to that of its salts, Table 1, is remarkable, for the difference between tetrachloro-p-benzoquinone⁵ and tetrachlorohydroquinone⁶ is only 200 kHz. It will be interesting to see if calculations considering the anion alone can account for the large reduction. The higher frequency

of the di-sodium salt over that of the barium salt does suggest that the cation might still be having some effect on the charge of the aromatic system. In the di-salt a metal-atom or proton is available to be associated with every oxygen, whereas in the mono-salt the cations can only be shared and thus their net proximity to oxygens will be less and thereby also their effect on the charge of the anion. The thorium, mercury and di-silver salts failed to give interactions.

Replacement of two of the chlorines in the quinoidal molecules with cyano groups leads to a one megahertz Cl^{35} NQR frequency increase, see 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in Table 1. The approximately forty kilohertz separation of its two interactions at 77°K becomes more than one-hundred kilohertz at room temperature. Typically splittings due to crystallographic differences become reduced with temperature increase as a gas-state conformation is approached. The thermal motions of the two chlorines of this molecule are apparently different and anisotropic.

The remaining molecule for discussion in Table 1, dimethytetrachloroterephthalate, appears to be the most interesting molecule located in this Thesis investigation. The temperature coefficient of the average of its Cl^{35} NQR frequencies, between liquid nitrogen and room temperature, is slightly positive. Further one of the interactions appears to exhibit a frequency increase of at least one megahertz, that is without precedence in carbon-chlorine NQR studies.

2. Inorganic Molecules

The first compound of Table 2, Cl_8BP , is the familiar complex, phosphorus (V) chloride-boron chloride^{7,8}. Conductance studies in

phosphoryl chloride have led to postulation of an ionic formulation⁸, $[\text{PCl}_4]^+ [\text{BCl}_4]^-$. Examination of the white solid at 77°K down to six megahertz revealed only the Cl^{35} interactions between 29 and 32.5 MHz, listed. It was outlined in Chapter V of this Thesis that the tetrachlorophosphonium ion exhibits Cl^{35} NQR in the frequency region 32.3 to 32.6 MHz. There are however the interactions about 29 MHz to be considered, but none in the range 20 to 25 MHz where tetrachloroborate Cl^{35} interactions might reasonably be expected and are predicted by CNDO calculations⁹. It appears most unlikely that any of the interactions observed are due to the boron-chlorine bond yet not all are attributable to the tetrachlorophosphonium ion. The spectrum of this compound is akin to that of ionic phosphoruspentachloride¹⁰ nevertheless it possesses the reported properties of the complex.

Selenyl chloride exhibits a remarkably intense and extensive chlorine NQR spectrum at 77°K. The eleven Cl^{35} interactions listed in Table 2 are of approximately equal intensity but differ in line-width. The average of these is barely two megahertz less than that of thionyl chloride for the same temperature. This is little considering the relative positions of sulphur and selenium in the atomic electronegativity scale. Although the complex spectrum probably results from crystallographic inequivalences, chloride transfer would result in the following ion pair, $^{11}[\text{SeOCl}]^+$ and $^{12}[\text{SeOCl}_3]^-$. An extensive review of the varied role of this molecule in complex formation is available¹³. Both selenium monochloride, Se_2Cl_2 , and diphenylselenium dichloride, $(\text{C}_6\text{H}_5)_2\text{SeCl}_2$, failed to exhibit quadrupolar interactions despite most extensive sample treatment and examination.

Table 2: NQR Spectra of Some Inorganic Chloride at 77°K, Frequencies in MHz.

	Cl^{35}	
Cl_8BP	32.448 32.275	slightly weaker than the others
$? (\text{PCl}_4^+ \text{BCl}_4^-)$	32.201 32.143 31.905	slightly weaker than the others
	28.996 28.946	twice as intense as the others
	Cl^{35}	Cl^{37}
Cl_9SSb	42.932	33.839
$(\text{SCl}_3^+ \text{SbCl}_6^-)$	42.185	33.250
	25.832	20.361
	22.308	17.593
	22.330	very broad and split
		24.810
		24.174 three similar strong
		24.269 broad interactions.
	Cl^{35}	Cl^{35}
SeOCl_2	31.122	30.452
selenyl chloride	30.868	30.421
	30.839	30.238
	30.781	30.168
	30.775	29.656
		29.176

The remaining compound of Table 2, Cl_9SSb , was prepared following the reported modification¹⁴ of an earlier procedure¹⁵ as an intermediate for synthesis in sulphur-nitrogen-phosphorus studies. Analysis for Cl, S and Sb was satisfactory. It is formulated as $[\text{SCl}_3]^+ [\text{SbCl}_6]^-$, evidence for this¹⁴ has been confirmed¹⁶ by examination of a sample from another preparation.

The higher frequency chlorine interactions already discussed in Chapter VI of this Thesis have been assigned to the $[\text{SCl}_3]^+$ ion. In the absence of structural information this assignment might be confirmed by examination of $^{17}\text{SCl}_3\cdot\text{AsF}_5$ and $^{16}(\text{SCl}_3)_2\cdot\text{SnCl}_6$ in which this cation is considered to be present, although there is incomplete agreement between the vibrational spectral assignments.

NQR studies of a variety of compounds known to contain the hexachloroantimonate ion¹⁸ and complexes of antimony pentachloride¹⁹, have led to definition of a frequency region for the Cl^{35} NQR of $[\text{SbCl}_6]^-$, that is (23.7 ± 0.7) MHz at 77°K. The remaining three Cl^{35} NQR frequencies listed for Cl_9SSb are most certainly from antimony-chlorine bonds, but not of $[\text{SbCl}_6]^-$ unless it is greatly distorted. Distortion of this anion would result in a finite electric field gradient at the antimony site and thus Sb^{121} and Sb^{123} NQR transitions of frequencies for each isotope approximating integral multiples modified by the asymmetry parameter²⁰.

The remaining three interactions, observed in the compound at about twenty-four megahertz, are broadened by application of a static magnetic field, indicating their origin from the nuclear magnetic phenomenon. They cannot be attributed to antimony quadrupolar interactions in the absence of others at a variety of frequencies defined by the quadrupole isotope ratio and their respective total nuclear angular momentum values. Temperature dependence studies can frequently assist in the identification of quadrupolar interactions, however the low NQR temperature coefficients of heavy

atoms at sites of high symmetry coupled in this case with the considerable breadth of the apparent interactions presents a worthless proposition. Although these three interactions are particularly intense, it is possible that their counterparts missed detection in searches from six to sixty megahertz, for it is reported that transitions from antimony at the same crystallographic site have exhibited considerable intensity difference¹⁹. In antimony NQR studies there are reports of unassignable interactions^{19,21} and of non-observation of predicted interactions²², thus the possible aberrance of this compound would not signify abnormality.

Dimeric arrangements, that have been frequently recognized in the solid antimony halides and that might occur amongst the atoms of Cl_9SSb through chlorine or sulphur bridging, are excluded on stoichiometric considerations. Without a complete structural determination more extensive NQR investigation needs to be undertaken to establish its proper formulation that this study does not confirm as $[\text{SbCl}_3]^+ [\text{SbCl}_6]^-$. The vibrational spectral studies of solid Cl_9SSb ^{14,16} are the justification for the inclusion of the cation¹⁷ in Chapter VI, that is independent of this uncertainty, for clearly the high frequency interactions will result from sulphur(IV)-chlorine bonds present in any reasonable formulation of the compound.

APPENDIX

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Statement of Contribution to Original Knowledge.⁺

The chlorine NQR frequencies of about one-hundred and fifty compounds have been discovered, their NQR spectra described and the frequencies determined and reported for one or more temperatures.

Through comparison of the observed spectra of groups of related molecules, interpretation of their chemical bonding is made and presented. The chlorine NQR spectra of some N-chloro molecules are interpreted to yield knowledge of their nitrogen atom orbital hybridization states. Their nitrogen-chlorine bond characters have been elucidated with the assistance of simple molecular orbital calculations. The observed spectra of some phosphorus chlorine molecules are interpreted to provide further information of phosphorus chemical bonding and for some, a knowledge of their stereochemistry. Through observation of the chlorine NQR spectra, the bonding of some cyclic inorganic molecules has been described and interpreted toward a knowledge of their respective structural conformations.

Studies of the temperature dependence of the Cl^{35} NQR spectra of three molecules are presented and interpreted. Curve fitting for two of these has led to the knowledge of probable lattice vibration frequencies and second-order phase transitions. Cl^{35} NQR line-width studies have yielded significant knowledge of the temperature of onset, nature, and potential barriers of hindered reorientational motions of their groups.

Chapter II has appeared as part of: Inorg. Chem., 8, 2431-2436 (1969)

Chapter III has appeared in: Canad. J. Chem., 48, 1976-1979 (1970)

Chapter IV is in press: Molec. Phys., 19, (3) (1970)

⁺ As required in Section 6(a) of "Information Concerning Theses", (Revised Feb. 1970), Thesis Office, Faculty of Graduate Studies and Research, McGill University